Journal of

ELECTROANALYTICAL CHEMISTRY

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

ELSEVIER

GENERAL INFORMATION

Types of contributions

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

Languages

Papers will be published in English, French or German.

Submission of papers

Papers should be sent to one of the following Editors:

Professor J. O'M. BOCKRIS, John Harrison Laboratory of Chemistry,
University of Pennsylvania, Philadelphia 4, Pa., U.S.A.
Professor G. MILAZZO, Istituto Superiore di Sanità,
Viale Regina Elena 299, Rome, Italy.
Professor C. N. REILLEY, Department of Chemistry,
University of North Carolina, Chapel Hill, N.C., U.S.A.

Authors should preferably submit two copies in double-spaced typing on pages of uniform size. Legends for figures should be typed on a separate page. The figures should be in a form suitable for reproduction, drawn in Indian ink on drawing paper or tracing paper, with lettering etc. in thin pencil. The sheets of drawing or tracing paper should preferably be of the same dimensions as those on which the article is typed. Photographs should be submitted as clear black and white prints on glossy paper.
All references should be given at the end of the paper. They should be numbered and the numbers should appear in the text at the appropriate places.
A summary of 50 to 200 words should be included.

Reprints

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

Publication

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

Subscription price (post free): £ 10.15.0 or $ 30.00 or Dfl. 108.00 per year; £ 5.7.6 or $ 15.00 or Dfl. 54.00 per volume.
The Abstracts Section can be obtained separately (post free) at the following prices: £.1.10.0 or $ 4.20 or Dfl. 15.00 per volume.

Additional cost for copies by air mail available on request.
For advertising rates apply to the publishers.

Subscriptions

Subscriptions should be sent to:

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

JOURNAL OF ELECTROANALYTICAL CHEMISTRY

VOL. 3 (1962)

JOURNAL *of* ELECTROANALYTICAL CHEMISTRY

INTERNATIONAL JOURNAL DEALING WITH ALL ASPECTS OF ELECTROANALYTICAL CHEMISTRY, INCLUDING FUNDAMENTAL ELECTROCHEMISTRY

Vol. 3 1962

ELSEVIER PUBLISHING COMPANY
AMSTERDAM

Printed in The Netherlands by
NEDERLANDSE BOEKDRUK INRICHTING N.V., 'S-HERTOGENBOSCH

REVUE GÉNÉRALE

LES INDICATEURS ELECTROCHIMIQUES

G. CHARLOT ET B. TRÉMILLON

Laboratoire de Chimie Analytique, 10 Rue Vauquelin, Paris V (France)

(Reçu le 12 juillet 1961)

Pour l'analyste qui doit réaliser un titrage, la détermination de la fin de la réaction, du point équivalent, est un problème d'un intérêt primordial. Cette détermination doit être aussi précise que possible, en principe plus précise que la mesure de la quantité de réactif mis en jeu pour le titrage. Mais en même temps, c'est la simplicité qui est le plus souvent recherchée. Dans cet esprit, et bien avant le développement des instruments de mesure, il a été fait appel à ce qu'il est convenu d'appeler les indicateurs de fin de réaction.

Comme son nom l'indique, un indicateur de fin de réaction est un composé qui permet, par échange d'une particule mise en jeu dans la réaction de titrage, de déterminer le point équivalent de celui-ci. Il existe divers types d'indicateurs selon la nature de la réaction envisagée: indicateurs de pH pour les réactions acides–bases, indicateurs d'oxydo-réduction, indicateurs de formation de complexes, de précipitation, pour les réactions du même type. C'est sous forme d'indicateurs colorés que ces composés ont été et sont toujours le plus couramment employés.

Supposons, par exemple, que l'on veuille titrer un acide par une base; nous ajoutons à la solution initiale d'acide un colorant ayant des propriétés acide–base, telles que ce colorant soit un acide plus faible que l'acide titré. Par addition de la base titrante, c'est l'acide à titrer qui réagit en premier lieu, la coloration restant ainsi invariable pendant tout le titrage. Au point équivalent, le colorant peut à son tour réagir, d'où un "virage", si les formes acide et base sont différemment colorées. Si la quantité d'indicateur ajoutée est très petite, 0.1% par exemple de la quantité d'acide à titrer, ce virage ne nécessite qu'une fraction très faible de base titrante, 0.1% de la quantité nécessaire pour atteindre le point équivalent. Celui-ci est ainsi mis en évidence visuellement, à 0.1% près. Cette condition essentielle exige naturellement une grande sensibilité de l'indicateur, c'est-à-dire que la coloration soit suffisamment intense pour être observée commodément aux faibles concentrations mises en jeu. Ce dernier point constitue d'ailleurs une limite de sensibilité à l'utilisation des indicateurs de fin de réaction pour les titrages de solutions diluées.

L'introduction des méthodes instrumentales — spectrophotométrie, conductimétrie, méthodes électrochimiques —, a permis par la suite d'envisager de nouvelles façons de déterminer la fin d'un titrage, par la mesure au cours de celui-ci de propriétés physico-chimiques de composés mis en jeu dans la réaction. Les concentrations de ces composés étant variables, le résultat de la mesure est lui-même variable et l'on peut tracer une courbe de titrage complète. Le but à atteindre est alors de mettre en évidence sur ces courbes le point équivalent, donc de choisir la méthode et les conditions qui fassent apparaître ce point comme un point singulier des courbes, déterminé avec la précision exigée du titrage. On peut alors parler de méthodes instrumentales "indicatrices", puisqu'elles peuvent indiquer en particulier la fin d'un titrage.

Mais ces méthodes instrumentales dites indicatrices ont permis également de nouveaux types d'indicateurs de réaction et, en particulier, des indicateurs électrochimiques. L'utilisation des méthodes électrochimiques qui permettent de suivre un titrage, telles que la potentiométrie et l'ampérométrie, est en effet limitée au cas où les corps mis en jeu dans la réaction sont électroactifs, pour donner lieu à une variation de potentiel d'électrode ou de courant d'électrolyse. Si aucun des composés n'est électroactif, il est cependant encore possible, comme dans le cas des indicateurs colorés, d'ajouter un corps électroactif qui permette, grâce à ses propriétés électrochimiques, de suivre des réactions variées — formation de complexes, précipitation, réactions acides-bases —, et plus particulièrement de mettre en évidence le point équivalent d'un titrage. Ce composé auxiliaire constitue ainsi un indicateur électrochimique. Ces indicateurs peuvent donner lieu, soit à des mesures potentiométriques — et on les nommera alors indicateurs potentiométriques —, soit à des mesures ampérométriques — et on les nommera indicateurs ampérométriques.

Après avoir examiné le cas des indicateurs potentiométriques et ampérométriques classiques, nous verrons que cette notion peut être maintenant genéralisée, apportant ainsi un ensemble de possibilités considérables.

INDICATEURS AMPÉROMÉTRIQUES ET POTENTIOMÉTRIQUES

Supposons que l'on veuille titrer par exemple des ions fluorure F^-. Différents réactifs titrants peuvent être utilisés: nitrates de thorium, Ca^{2+} (qui forment des fluorures peu solubles), Al^{3+} (qui forme des complexes AlF_6^{3-}). Aucun de ces composés n'est électroactif et ne permet de suivre directement le titrage par ampérométrie ou potentiométrie.

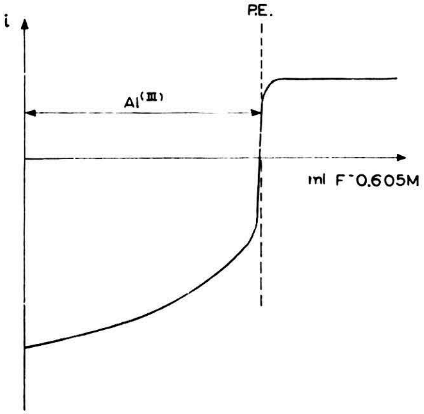


Fig. 1. Titrage ampérométrique de Al(III) par F^-, avec Fe^{3+} comme indicateur. Al(III) 10^{-2} *M* + Fe(III) $8\cdot10^{-4}$ *M* + alcool 50% + NaCl en excès. Electrode à gouttes de mercure court-circuitée avec une électrode au calomel. (D'après A. RINGBOM ET B. WILKMAN[3].)

Mais les ions Fe^{3+}, qui forment des complexes ferrifluorure, sont électroactifs et peuvent donc servir d'indicateur. On ajoute à la solution un peu de Fe(III) et on suit par exemple la variation du courant de réduction à une électrode de platine ou de mercure de potentiel convenable (0.25 V, potentiel que prend une électrode court-circuitée avec une électrode au calomel et KCl saturé). Avant le point équivalent, le courant est sensiblement nul (courant résiduel), Fe(III) restant sous forme de complexe. Après le point équivalent, un excès du réactif, qui forme avec F^- un complexe plus stable que le ferri-fluorure, détruit celui-ci et libère Fe^{3+}. Le courant de réduction croît. Inversement, on peut titrer Th(IV)[1], Al(III), Mg(II) et Ca(II)[2,3] par du fluorure de sodium en présence de Fe^{3+} comme indicateur. Fe^{3+} ne réagit en principe qu'après le point équivalent. Il y a donc diminution du courant de réduction à ce moment (Fig. 1). Le montage est particulièrement simple, puisqu'il n'est besoin d'imposer aucune tension entre électrodes.

Fe^{3+} a été utilisé ici comme indicateur ampérométrique. Seul, il ne peut servir d'indicateur potentiométrique, car le potentiel mesuré serait un potentiel mixte instable, pratiquement inutilisable. Mais en présence du réducteur correspondant Fe^{2+}, une électrode de platine prend un potentiel d'équilibre:

$$E_{eq} = E_0 + 0.06 \log \frac{[Fe^{3+}]}{[Fe^{2+}]}$$

dont la valeur est indicatrice de F^- par suite de la formation de ferri-fluorure. On peut ainsi suivre potentiométriquement le titrage de F^-, ou au contraire le titrage de Pb^{2+} par exemple, par F^- [4]. En présence de chlorure, Pb(II) précipite sous forme PbFCl. Avant le point équivalent, le potentiel reste élevé (Fe^{3+} non complexé). Puis, au point équivalent, il diminue brusquement (Fe^{3+} complexé par l'excès de fluorure) (Fig. 2). Le système Fe^{3+}/Fe^{2+} a été utilisé comme indicateur potentiométrique.

Différents autres systèmes dont les caractéristiques électrochimiques varient au point équivalent peuvent de la même façon être utilisés comme indicateurs potentio-

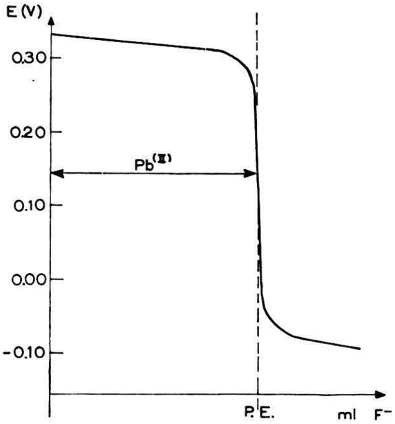


Fig. 2. Titrage potentiométrique à intensité nulle de Pb(II) par F^- en présence de chlorure, avec $Fe^{+3} + Fe^{2+}$ comme indicateurs. (D'après L. FARKAS ET N. VRI[4].)

métriques ou ampérométriques de la fin d'un titrage. Par exemple, l'eau oxygénée a été utilisée pour des titrages d'acide chlorhydrique par la soude et inversement[5-7] (Fig. 3). La mise en évidence du point équivalent est basée sur le fait que les réactions électrochimiques auxquelles H_2O_2 participe (oxydation en oxygène, réduction en eau ou HO^-) sont lentes en milieu acide et neutre et assez rapides en milieu alcalin (voir[8] p. 94).

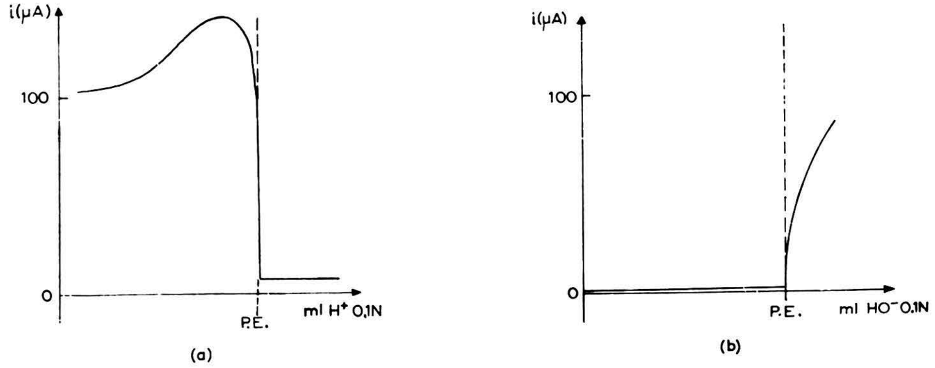


Fig. 3. Titrage ampérométrique à deux électrodes indicatrices de platine, $\Delta E = 10$ mV; (a) soude titrée par HCl; (b) HCl titré par la soude; eau oxygénée $1^0/_{00}$ environ comme indicateur (d'après D. R. Clippinger et C. W. Foulk[5]; reproduit de H. L. Kies, *Thèse*, Delft, 1956).

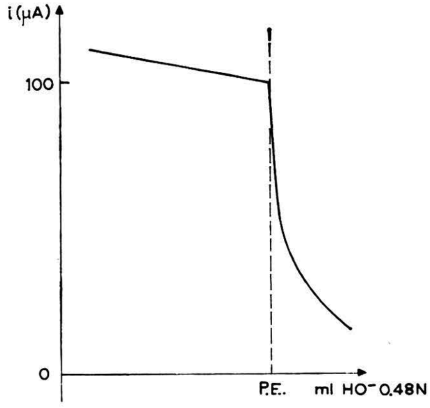


Fig. 4. Titrage ampérométrique de HCl 0.485 *N* par la soude, en présence de I_3^- 10^{-3} *M* comme indicateur. Deux électrodes indicatrices de platine, $\Delta E = 10$ mV (d'après H. L. Kies, *Thèse*, Delft, 1956).

Un autre système indicateur est constitué par les composés de l'iode, $I^-/I^0/IO_3^-$ [5-7]. En effet, en milieu acide, I_3^- est stable et la réaction électrochimique $I_3^- + 2e \rightleftharpoons 3\ I^-$ peut avoir lieu, dans les deux sens à des potentiels voisins, car elle est rapide. Au contraire, en milieu alcalin, l'iode se dismute en iodate et iodure et les réactions électrochimiques qui peuvent se produire sont, à l'anode, l'oxydation de l'iodure en iodate et, à la cathode, la réduction de l'iodate en iodure. Ces deux réactions ont lieu à des potentiels très différents car le système $IO_3^- + 3\ H_2O + 6\ e \rightleftharpoons I^- + 6\ HO^-$ est lent.

Pour suivre un titrage d'une base par un acide, on ajoute donc $I^- + IO_3^-$ comme indicateurs. Après le point équivalent, $I^- + IO_3^-$ donnent de l'iode. Par exemple, la courbe de titrage ampérométrique à deux électrodes indicatrices est représentée Fig. 4[6]. Inversement, pour titrer un acide par une base, on ajoute un peu d'iode qui se dismute après le point équivalent en $I^- + IO_3^-$.

Ces exemples montrent que les indicateurs électrochimiques doivent répondre à la caractéristique commune à tous les indicateurs: provoquer la variation brusque d'une propriété au point équivalent du titrage. Si nous examinons plus précisément les conditions qu'ils doivent remplir pour atteindre ce but, nous constatons que:

(1) Comme pour tous les indicateurs, ils ne doivent réagir avec le réactif titrant qu'à partir du point équivalent, et leur quantité doit être négligeable devant celle du corps titré pour que la variation brusque de propriété, due à la fin de réaction de l'indicateur, ait lieu pratiquement au point équivalent.

(2) Cette seconde condition vient limiter l'utilisation des indicateurs électrochimiques dans le domaine des concentrations. En effet, il existe une limite de concentration de l'indicateur en-dessous de laquelle celui-ci n'est plus électroactif et par conséquent ne provoque plus de variation de la grandeur mesurée, de même qu'il existe une limite de concentration des indicateurs colorés en-dessous de laquelle la solution n'est plus assez colorée pour que l'œil observe une modification. On sait que cette concentration limite, due à l'existence du courant résiduel et de phénomènes électriques et électrochimiques parasites, est généralement de l'ordre de 10^{-4} *M* environ. Un indicateur électrochimique ne permet donc de déterminer un point équivalent à moins de 1% près qu'à condition que la solution du corps à titrer soit au moins 10^{-2} *M*.

GÉNÉRALISATION — LES RÉACTIONS ÉLECTROCHIMIQUES INDICATRICES

En réalité, les méthodes instrumentales offrent des possibilités considérables et leur exploitation permet d'étendre l'emploi des composés électroactifs pour suivre les titrages mettant en jeu des corps non-électroactifs. Nous allons passer en revue les différents moyens.

(A) En premier lieu, on peut s'affranchir de la limite de sensibilité vue précédemment pour l'utilisation des indicateurs, soit que le tracé de la courbe de titrage permette de déterminer le début de réaction de l'indicateur, soit que l'on ne puisse titrer

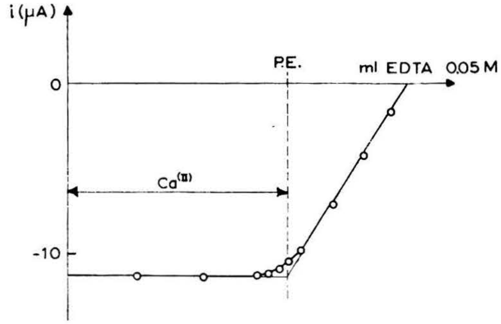


Fig. 5. Titrage ampérométrique par l'EDTA avec ZnO_2^{2-} 0.002 *M* comme indicateur. Une électrode indicatrice à gouttes de mercure: *E* = —1.5 V. 5.5 mg de Ca(II). (D'après H. A. LAITINEN ET R. F. SYMPSON[9].)

que la quantité totale corps à doser + indicateur mais que l'on connaisse la quantité de ce dernier (dosage par différence).

La Fig. 5 représente un exemple d'application de la première méthode. En milieu alcalin, les ions Ca^{2+} donnent avec l'EDTA un complexe plus stable que celui formé par les ions zincate $ZnO_2{}^{2-}$. Ces derniers sont réductibles à une électrode de mercure et permettent de suivre ampérométriquement le titrage. A l'échantillon de Ca(II) à titrer, on ajoute donc $ZnO_2{}^{2-}$ en présence de 100 à 140 fois plus d'ions HO^- et l'on titre par l'EDTA. Avant le point équivalent, seul Ca(II) réagit et le courant de réduction à —1.5 V reste constant. Après le point équivalent, Zn(II) réagit et le courant diminue[9]. Les mêmes phénomènes ont lieu en milieu ammoniacal[10]. Au contraire de Ca(II), Mg(II) forme avec l'EDTA dans les mêmes milieux un complexe moins stable que Zn(II). D'où une possibilité de titrer Ca(II) en présence de Mg(II)[9,10].

Si l'on connaît la quantité de l'indicateur — suffisante pour qu'il soit électroactif, on peut alors se contenter de déterminer la fin de réaction de celui-ci. Par exemple, la précipitation de l'oxalate de calcium a été suivie avec Cd^{2+} comme indicateur ampérométrique[3]. CdC_2O_4 précipite simultanément avec CaC_2O_4. Il faut donc ajouter une quantité connue de Cd(II) et on titre la somme Ca(II) + Cd(II) par l'oxalate, en suivant le courant de réduction à une électrode à gouttes de mercure de potentiel $E = -0.55$ V. Au point équivalent, le courant devient égal au courant résiduel (Fig. 6).

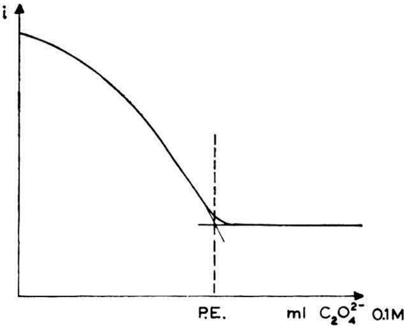


Fig. 6. Titrage ampérométrique de Ca^{2+} 10^{-2} *M* par l'oxalate, avec Cd^{2+} $8 \cdot 10^{-4}$ *M* comme indicateur. Milieu: éthanol 50%. Une électrode à gouttes de mercure: $E = -0.55$ V. (D'après A. Ringbom et B. Wilkman[3].)

Il n'est pas nécessaire de connaître la quantité d'indicateur ajouté; elle peut être déterminée par un pré-titrage. Par exemple, Ca(II) ou Zn(II) peuvent être titrés par l'EDTA en milieu ammoniacal, à l'aide de mercure(II) comme indicateur électrochimique[11,12]. Dans la cellule de titrage, on introduit une petite quantité de Hg(II) que l'on pré-titre par l'EDTA avant d'introduire l'échantillon à doser, par exemple de Zn(II). Après ce pré-titrage, Zn(II) — qui forme avec l'EDTA un complexe plus stable, dans le milieu choisi, que Hg(II) —, réagit avec tout l'EDTA introduit jusqu' alors et libère l'indicateur. On titre ensuite jusqu'à la fin de réaction de celui-ci et la différence entre les deux points équivalents fournit le titre de l'échantillon ajouté (Fig. 7).

On peut encore, au lieu d'ajouter Hg(II) puis de le pré-titrer par l'EDTA, ajouter directement le complexe Hg^{2+}–EDTA, puis l'échantillon de l'élément à doser (formant avec l'EDTA un complexe plus stable que celui formé par Hg(II)), et titrer par l'EDTA jusqu'au point équivalent, qui donne cette fois directement le titre de l'échantillon[13,14] (Fig. 8).

La quantité d'indicateur peut être maintenant importante, du même ordre de grandeur que celle du corps titré, et même supérieure à celle-ci. La limite de sensibilité des titrages est ainsi reculée jusqu'à celle des titrages potentiométriques et ampérométriques directs.

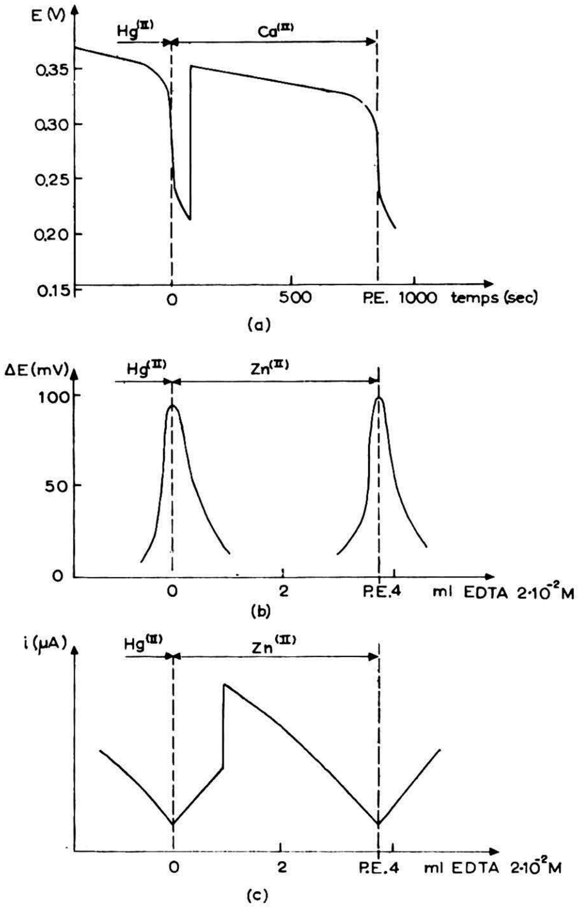


Fig. 7. Titrages par l'EDTA, avec Hg(II) pré-titré comme indicateur. (a) Titrage coulométrique à intensité constante de Ca(II), tampon ammoniacal, pH 8.5; potentiométrie à intensité nulle avec une électrode de mercure indicatrice. (D'après C. N. REILLEY ET W. W. PORTERFIELD[12].) (b) et (c) Titrage de Zn(II) 10^{-3} M, tampon citrate, pH 4.4; deux électrodes indicatrices d'or amalgamé, potentiométrie à intensité constante de 6.3 μA (b) et ampérométrie à différence de potentiel constante de 10 mV. (D'après G. GUÉRIN, J. DESBARRES ET B. TRÉMILLON[11].)

(B) *Electrodes métalliques indicatrices de corps non électroactifs*

On sait que la courbe intensité–potentiel d'oxydation d'un métal peut subir un déplacement dans l'échelle des potentiels selon le milieu dans lequel cette oxydation a lieu. Si la réaction d'oxydation est symbolisée par M$\downarrow$ — ne $\rightarrow$ M (degré d'oxydation $+ N$), le potentiel normal de cette réaction dépend de la forme réelle sous laquelle le degré d'oxydation $+ N$ existe en solution. Si celle-ci contient un agent complexant, le potentiel normal est d'autant moins élevé que le complexe est plus stable.

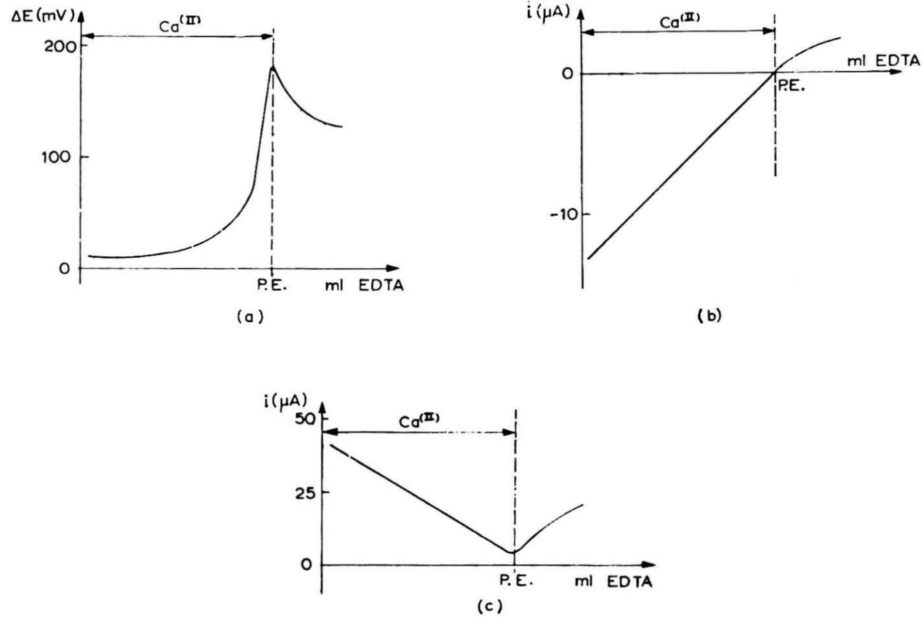


Fig. 8. Titrage de Ca(II) par l'EDTA, avec le complexe Hg^{2+}–EDTA comme indicateur. Hg^{2+}–EDTA $3.5 \cdot 10^{-3}$ M, Ca^{2+} 10^{-3} M, tampon ammoniacal 0.1 M, pH 9.3. (a) potentiométrie à intensité constante de 10 μA, deux électrodes indicatrices de mercure; (b) ampérométrie avec une seule électrode indicatrice, $E = 0.20$ V; (c) ampérométrie avec deux électrodes indicatrices, $\Delta E = 200$ mV. (D'après A. E. MARTIN ET C. N. REILLEY[13].)

Par exemple, en présence d'EDTA, le mercure est oxydable selon la réaction électrochimique:

$$\mathrm{Hg}\downarrow + \mathrm{Y} - 2\mathrm{e} \leftrightharpoons \mathrm{HgY} \qquad (1)$$

Y symbolise l'EDTA et les anions basiques correspondants et HgY symbolise le complexe mercurique. Le potentiel normal E_1 du système est:

$$E_1 = E_0 + 0.029 \log K$$

K étant la constante conditionnelle de dissociation, variable en particulier avec le pH de la solution, du complexe HgY:

$$K = \frac{[\mathrm{Y}][\mathrm{Hg}^{2+}]}{[\mathrm{HgY}]}$$

et E_0, le potentiel normal du système Hg$\downarrow$ — 2e $\rightleftharpoons$ Hg^{2+} ($E_0 = 0.85$ V).

La réaction (1) peut se produire à des potentiels moins élevés que ceux où a lieu l'oxydation du mercure en l'absence d'EDTA.

On peut mettre en évidence sur les courbes expérimentales, des parties correspondant à la production de cette réaction et dépendant par conséquent de la présence de l'EDTA, composé non électroactif[11,15-17].

La Fig. 9 représente par exemple de telles courbes intensité–potentiel pour différentes valeurs de pH. Sur ces courbes, apparaissent des vagues correspondant à la réaction électrochimique (1) et, notamment, des paliers de diffusion de hauteur proportionnelle à la concentration de l'EDTA en solution[8]. Une mesure d'intensité de courant à une électrode de mercure portée à un potentiel correspondant à ce palier est donc indicatrice de concentration de l'EDTA. De même, le potentiel que prend l'électrode de mercure à intensité (d'oxydation) imposée est indicateur de concentration de l'EDTA, si cette intensité reste inférieure à la hauteur du palier de diffusion. On peut dire que l'électrode de mercure est indicatrice de concentration d'un composé non électroactif, l'EDTA, et permet ainsi de suivre des titrages qui mettent en jeu ce composé.

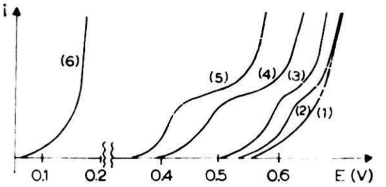


Fig. 9. Courbes intensité–potentiel d'oxydation du mercure en présence d'EDTA ($4 \cdot 10^{-4}$ *M*). Electrode fixe de mercure: pH de la solution. 0.8 (1), 1.2 (2), 1.8 (3), 3.6 (4), 4.8 (5) et 9.2 (6). (D'après G. Guérin, J. Desbarres et B. Trémillon[11].)

Remarques: (1) En ce qui concerne le potentiel pris par l'électrode à intensité nulle, il s'agira d'un potentiel mixte, mal défini, si la solution ne contient pas de complexe HgY. Au contraire, en présence de complexe HgY, en concentration suffisante pour que le potentiel pris par l'électrode ne soit plus un potentiel limite mais un véritable potentiel d'équilibre (voir[8,18]), on a:

$$E_{eq} = E_1 + 0.029 \log \frac{|\mathrm{HgY}|}{|\mathrm{Y}|}$$

(2) Il faut naturellement que la réaction électrochimique soit suffisamment rapide pour pouvoir utiliser un tel système indicateur. Il a été ainsi montré par exemple qu'une électrode de cuivre ne peut être indicatrice de concentration de l'EDTA, la réaction électrochimique $\mathrm{Cu}\downarrow + \mathrm{Y} - 2e \rightleftharpoons \mathrm{CuY}$ étant trop lente pour avoir lieu en pratique[11].

Il existe de nombreux exemples analogues. En présence d'un halogénure X^-, l'argent est oxydable selon la réaction électrochimique:

$$\mathrm{Ag}\downarrow + \mathrm{X}^- - e \rightleftharpoons \mathrm{AgX}\downarrow$$

La Fig. 10 représente les courbes intensité–potentiel obtenues par voltammétrie à une électrode d'argent en présence de Cl^-, Br^- ou I^-[19]. Il apparaît une vague d'oxydation, dont le palier est dû à la limite de diffusion de l'halogénure et dont la hauteur est, par conséquent, proportionnelle à la concentration de celui-ci.

L'électrode se trouve automatiquement recouverte d'halogénure insoluble. A intensité nulle, le potentiel qu'elle indique est un potentiel d'équilibre fonction de la concentration de X^- libre:

$$E_{eq} = E_1 - 0.059 \log |X^-|$$

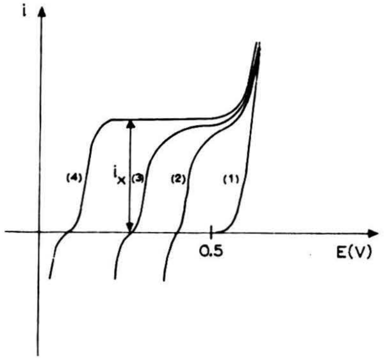


Fig. 10. Courbes intensité–potentiel d'oxydation de l'argent en présence d'halogénures. Concentrations: $HClO_4$ N (1); $HClO_4$ N + Cl^- 10^{-3} M (2); $HClO_4$ N + Br^- 10^{-3} M (3); $HClO_4$ N + I^- 10^{-3} M (4). (D'après J. BADOZ-LAMBLING[19]; reproduit de G. CHARLOT, J. BADOZ-LAMBLING ET B. TRÉMILLON[8].)

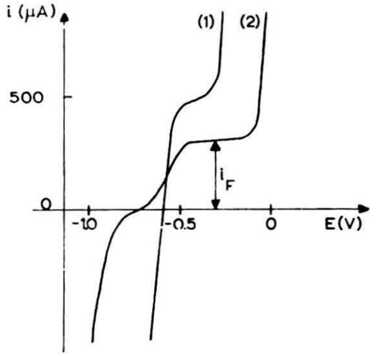
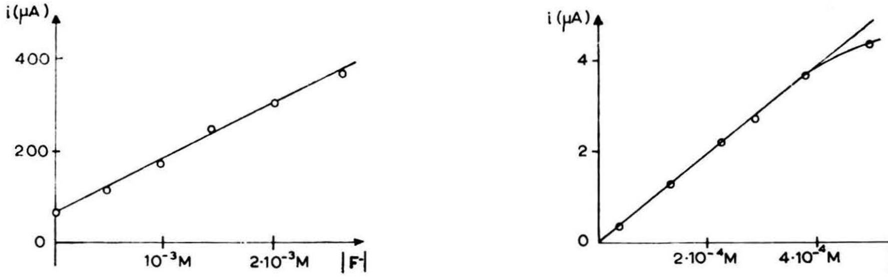


Fig. 11. Courbes intensité–potentiel d'oxydation de l'aluminium en présence de fluorure ($4 \cdot 10^{-3}$ M) — pH 1 (1) et 3 (2). (D'après N. DUMONTIER-GOUREAU ET B. TRÉMILLON[23].)

L'électrode d'argent est indicatrice de concentration des halogénures, bien que les propriétés réductrices de ces anions ne soient pas utilisées ici.

L'électrode d'argent est encore indicatrice de concentration des ions sulfure, cyanure, hydroxyde (pH) . . . L'électrode de mercure également est indicatrice de concentration de sulfure, cyanure, halogénures[20,21]. De nombreux métaux sont indicateurs de concentration de HO^- par suite de formation d'hydroxydes insolubles; l'aluminium est indicateur de F^- [22–25] (Figs. 11 et 12).



(a)

(b)

Fig. 12. Electrode d'aluminium indicatrice de concentration de F^-. (a) Cellule $Al\downarrow/F^-$ (pH 3), O_2 saturé/$Pt\downarrow$; les deux électrodes sont court-circuitées. (D'après N. DUMONTIER-GOUREAU ET B. TRÉMILLON[23].) (b) Cellule $Al\downarrow/F^-$(pH 3.6)/Cl^- sat./$Hg_2Cl_2\downarrow/Hg\downarrow$; tension entre les deux électrodes —0.75 V; électrode d'aluminium tournante. (D'après I. M. KOLTHOFF ET J. SAMBUCETTI[25].)

Toutes ces électrodes métalliques constituent des indicateurs électrochimiques d'un genre particulier; elles permettent de suivre un titrage mettant en jeu le composé non électroactif dont elles sont indicatrices, sans intervenir chimiquement dans la réaction de titrage. Nous donnons quelques exemples d'application.

La Fig. 13 représente un titrage d'un cation métallique non électroactif par l'EDTA, avec une électrode de mercure indicatrice de l'EDTA. L'apparition, après le point équivalent, d'un excès d'EDTA provoque la naissance d'une vague d'oxydation du mercure, que l'on utilise pour localiser le point équivalent[14,26]. Par exemple, pour titrer un mélange de bismuth(III), plomb(II) et calcium(II)[26], Bi(III) et Pb(II) sont prédéterminés par ampérométrie directe en mesurant le courant de réduction de Bi^{3+} et Pb^{2+} à une électrode de mercure de potentiel imposé. Ensuite, imposant à l'électrode un potentiel de +0.30 V, le titrage de Ca^{2+} est effectué. Après le point équivalent, l'EDTA en excès permet le passage d'un courant d'oxydation, $Hg\downarrow + Y - 2e \rightarrow HgY$, proportionnel à la concentration de Y libre.

L'électrode d'argent est, comme nous l'avons vu, indicatrice de concentration d'anions divers, halogénures, sulfure, cyanure, thiocyanate, etc. Elle permet donc de suivre des titrages de cations métalliques par ces anions, par exemple: titrage de Ni^{2+} par CN^- (formation quantitative de $Ni(CN)_4^{2-}$), par potentiométrie à intensité nulle[27,28] ou ampérométrie à deux électrodes indicatrices (Fig. 14); ou encore, titrage de Hg^{2+} par SCN^- (formation de $Hg(SCN)_2\downarrow$) par potentiométrie à intensité nulle[29].

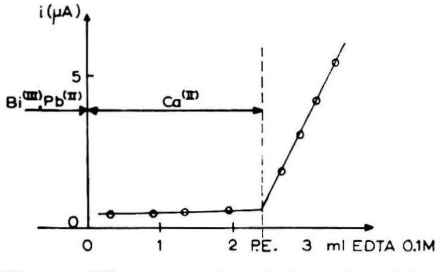


Fig. 13. Titrage ampérométrique du calcium par l'EDTA, avec une électrode de mercure indicatrice. $E = +0.30$ V. (D'après C. N. REILLEY, W. G. SCRIBNER ET C. TEMPLE[26].)

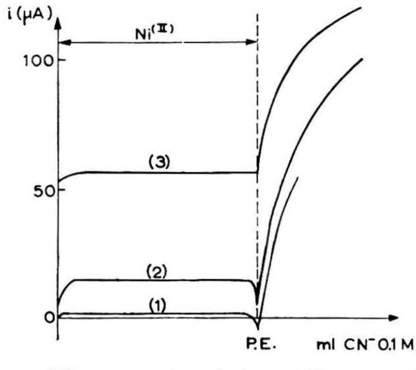


Fig. 14. Titrage ampérométrique de Ni^{2+} $5 \cdot 10^{-2}$ M par le cyanure, en tampon ammoniacal 1 M, avec deux électrodes indicatrices d'argent; ΔE = 20 mV (1), 100 mV (2), 250 mV (3) (D'après M. RUMEAU).

L'existence d'une vague d'oxydation de l'aluminium en présence d'ions F^-, en milieu peu acide, a conduit à utiliser une électrode de ce métal pour suivre, ampérométriquement, le titrage des fluorures par Th(IV), Al^{3+}, Ca^{2+}, Mg^{2+}, etc. ou inversement de ces éléments par F^- [30,31] (Fig. 15).

Des titrages acides–bases peuvent également être suivis à l'aide d'électrodes indicatrices de ce type. L'électrode à hydrogène, qui utilise l'électroactivité des ions H^+ ou de leurs complexes, les acides, est d'un emploi peu répandu parce que délicat et mal commode. On utilise plus couramment, pour suivre les titrages acides–bases, une électrode en verre, dont le potentiel de membrane varie avec l'activité des ions H^+. Mais, en raison de la grande résistance de cette électrode, son utilisation est limitée à la potentiométrie à intensité nulle. Pour les autres types de titrages voltammétriques, on doit faire appel à des systèmes électrochimiques indicateurs, c'est-à-dire dans lesquels les ions H^+ interviennent sans changement de degré d'oxydation.

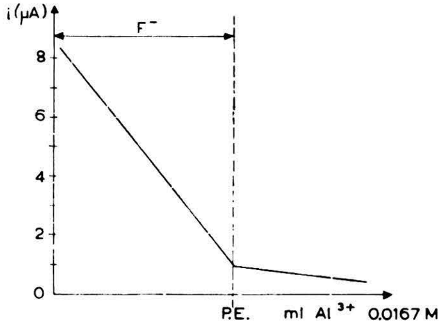


Fig. 15. Titrage ampérométrique de F^- $5 \cdot 10^{-4}$ *M* par le nitrate d'aluminium. Milieu: éthanol 50%, NO_3^- 0.5 *M*, pH 4.0 (acétique). Une électrode indicatrice d'aluminium tournante: $E = -0.50$ V. (D'après I. M. KOLTHOFF, E. J. MEEHAN ET C. J. SAMBUCETTI[31].)

Tous les métaux formant des hydroxydes, $M^{n+} + n\,HO^- \rightleftharpoons M(OH)_n$, sont en principe indicateurs de pH, si le système électrochimique:

$$M\downarrow + n\,HO^- - n\,e \rightleftharpoons M(OH)_n$$

peut être mis en évidence. Il en est de même si la réaction conduit à des ions basiques $M(OH)_p^{(n-p)+}$ ou $M(OH)_q^{(q-n)-}$ (soit encore $MO_{q/2}^{(q-n)-}$).

Sur ce principe, de nombreux éléments ont pu être utilisés pour les mesures de pH. Nous rappelons seulement pour mémoire l'utilisation extensive de l'antimoine, mais également, du tellure, du zirconium, de l'argent, du mercure. Récemment, et plus complètement, fut étudié le comportement de l'aluminium pour ce type de déter-

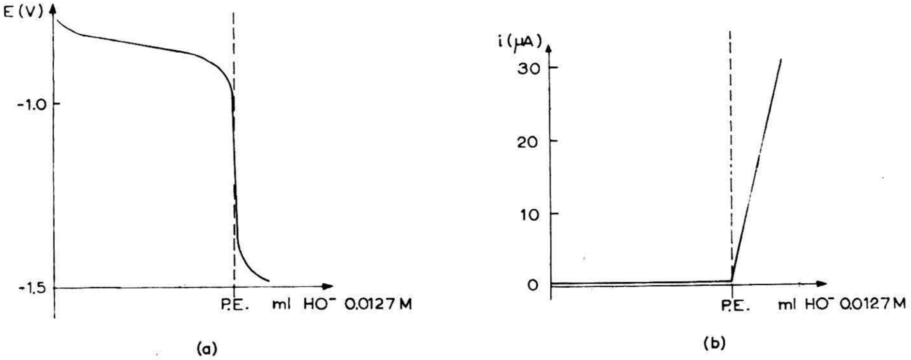


Fig. 16. Titrage (a) potentiométrique à intensité nulle, (b) ampérométrique, de biphtalate de potassium 0.00127 *M* par la soude. Une électrode d'aluminium indicatrice. $E = -0.75$ V pour l'ampérométrie. (D'après I. M. KOLTHOFF ET C. J. SAMBUCETTI[32].)

minations[23,24,32,33–35]. Ce comportement est loin d'être idéal du point de vue strictement théorique.

En effet, en milieu peu acide à peu basique, l'aluminium est oxydable en alumine, insoluble, qui se forme à la surface de l'électrode et a la propriété de passiver celle-ci. Les phénomènes ne sont alors plus prévisibles théoriquement. En milieu alcalin, l'aluminium est oxydé en aluminate AlO_2^-, soluble, d'où des phénomènes beaucoup plus reproductibles. D'autre part, d'autres composés en solution, tels les fluorures, les phosphates, peuvent influer notablement sur l'oxydation du métal et interférer avec les ions HO^- [32]. En réalité, les électrodes métalliques de ce type sont plus exactement indicatrices des ions HO^-.

Néanmoins, il est possible de suivre ainsi des titrages acides–bases, puisqu'une différence très importante entre les phénomènes électrochimiques intervient quand on passe des milieux acides aux milieux alcalins. La Fig. 16, par exemple, représente les courbes de titrages potentiométrique à intensité nulle et ampérométrique, à une seule électrode indicatrice d'aluminium, du biphtalate de potassium par la soude.

(C) *Indicateurs complexes*

Nous avons déjà dit qu'une électrode de mercure, en présence du complexe HgY, peut prendre un potentiel d'équilibre indicateur de concentration de l'EDTA libre:

$$E_{eq} = E_0 + 0.029 \log \frac{[HgY]}{[Y]}$$

et, si $|HgY| = C^{te}$:

$$E_{eq} = C^{te} - 0.029 \log [Y]$$

Ce potentiel d'équilibre permet de suivre la réaction entre l'EDTA et un cation métallique M^{2+} non électroactif. Puisque:

$$\frac{[M^{2+}][Y]}{[MY]} = K$$

l'expression du potentiel d'équilibre peut prendre la forme:

$$E_{eq} = C^{te} - 0.029 \log \frac{[MY]}{[M^{2+}]}$$

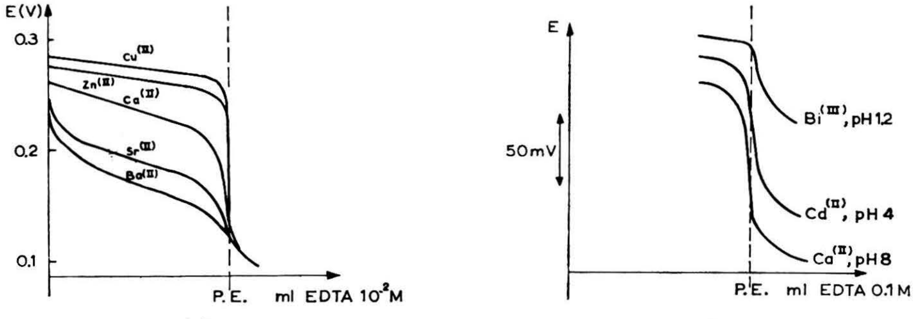
E_{eq} est fonction de la concentration de deux composés non électroactifs. La constante dépend de la stabilité (K) du complexe MY.

Des titrages par potentiométrie à intensité nulle avec une électrode indicatrice de mercure ont été ainsi réalisés pour de très nombreux éléments[12,36–41]. La Fig. 17a représente le titrage de Cu(II), Zn(II), Ca(II), Sr(II) et Ba(II) en milieu tampon ammoniacal, pH 9.2[37]. En choisissant convenablement le pH de la solution à titrer, on peut jouer sur la stabilité apparente des complexes pour titrer certains éléments tandis que d'autres ne réagissent pas. Les titrages sont ainsi rendus plus sélectifs[38] (Fig. 17b). D'autres agents complexants peuvent encore permettre d'améliorer la sélectivité[36].

A la place d'électrodes de mercure, on peut utiliser des électrodes solides amalgamées (platine, or, argent . . .) qui se comportent de façon identique[11,38,39,40].

Si de plus, $[MY] = C^{te}$, le potentiel d'équilibre devient:

$$E_{eq} = C^{te} + 0.029 \log[M^{2+}]$$



(a) (b)

Fig. 17. Titrages potentiométriques à intensité nulle avec une électrode de mercure et le complexe HgY comme indicateurs. (a) Titrages de Cu(II), Zn(II), Ca(II), Sr(II), Ba(II) en tampon ammoniacal, pH 9.2. (D'après C. N. REILLEY ET R. W. SCHMID[37]); (b) Titrages de Bi(III) + Cd(II) + Ca(II) à divers pH. (D'après C. N. REILLEY, R. W. SCHMID ET D. W. LAMSON[38].)

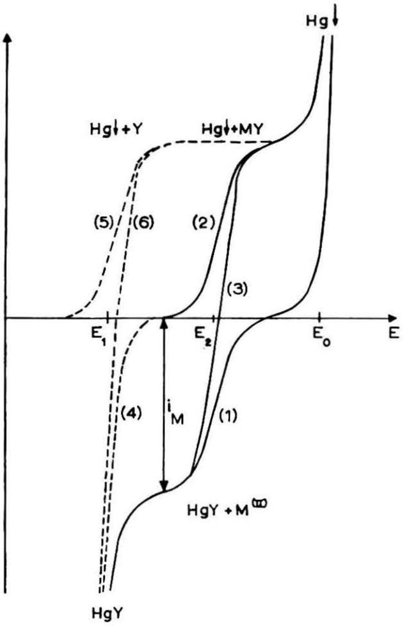


Fig. 18. Indicateurs électrochimiques. Courbes $i = f(E)$ à une électrode de mercure: (1) M(II) + HgY en excès; (2) MY seul; (3) M(II) + MY + HgY en excès. Courbes en pointillé: (4) HgY; (5) Y; (6) Y + HgY (courbes théoriques).

Il n'est plus fonction que de la concentration du cation métallique M^{2+}. Le système électrode de mercure/HgY + MY est indicateur (potentiométrique) de M^{2+} et permet de suivre la réaction de M^{2+} avec un autre composé non électroactif. Ce système constitue un indicateur complexe. Par exemple, la mesure du potentiel indiqué par une électrode de mercure en présence de $HgY + MgY$ a permis de suivre la formation d'oxalate de magnésium[42]. D'autres exemples d'indicateurs potentiométriques complexes peuvent être cités: le système amalgame de plomb/$PbC_2O_4\downarrow + CaC_2O_4\downarrow$ est indicateur de concentration de Ca^{2+} et a permis de suivre la formation du complexe calci–citrique $Ca(C_5H_6O_7)^-$[43]; le système $Hg\downarrow/HgY + ZnY$ est indicateur de concentration de Zn^{2+} et permet de suivre la formation par exemple des complexes Zn(II)–citrate; le système $Pt\downarrow$/ferricyanure $Fe(CN)_6^{3-}$ + ferrocyanure de zinc $Zn_3K_2[Fe(CN)_6]_2\downarrow$ est également indicateur de concentration de Zn^{2+}, etc. La mise en jeu d'indicateurs complexes de cette sorte permet de multiplier considérablement les applications.

Ces systèmes complexes peuvent également servir d'indicateurs ampérométriques. En effet, les courbes intensité–potentiel théoriques (Fig. 18) correspondant aux systèmes $Hg\downarrow/HgY$, $Hg\downarrow/HgY + MY$, $Hg\downarrow/HgY + M^{2+}$ (HgY plus stable que MY) font apparaître deux groupes de vagues, les unes correspondant à la réaction:

$$Hg\downarrow + Y - 2\,e \rightleftharpoons HgY$$

les autres à une nouvelle réaction électrochimique:

$$Hg\downarrow + MY - 2\,e \leftrightharpoons HgY + M^{2+}$$

qui se produit à des potentiels intermédiaires entre ceux où les réactions $Hg\downarrow - 2\,e \rightleftharpoons Hg^{2+}$ et $Hg\downarrow + Y - 2\,e \rightleftharpoons HgY$ ont lieu (réactions supposées rapides). On remarque alors que le système $Hg\downarrow/HgY$ peut être indicateur ampérométrique de M^{2+}, puisqu'un courant de réduction fonction de la concentration des ions M^{2+} existe dans cette zone intermédiaire de potentiel.

La quinhydrone, que l'on peut considérer comme un mélange de benzoquinone et d'hydroquinone, est un indicateur complexe semblable, comme le montrent les courbes intensité–potentiel[44,45]. La benzoquinone est réductible en hydroquinone, à une électrode de platine par exemple:

$$\text{benzoquinone} + 2\,e \rightleftharpoons \text{hydroquinone}$$

La quinone étant symbolisée par Q, l'hydroquinone est symbolisée par H_2Q. Le système oxydo-réducteur ci-dessus fait donc intervenir des protons. En réalité, l'hydroquinone est un acide faible et l'on a, selon le domaine de pH, les différentes réactions électrochimiques possibles:

$$\begin{aligned}
&\text{pH} > 12 &&: Q + 2\,e \rightleftharpoons Q^{2-}\\
&\text{pH } 9 \text{ à } 12 &&: Q + H_2O + 2\,e \rightleftharpoons HQ^- + HO^-\\
&\text{pH } 7 \text{ à } 9 &&: Q + 2\,H_2O + 2\,e \rightleftharpoons H_2Q + 2\,HO^-\\
&\text{pH} < 7 &&: Q + 2\,H^+ + 2\,e \rightleftharpoons H_2Q
\end{aligned}$$

On voit qu'en milieu acide par exemple, la réduction de Q nécessite la présence de deux protons; leur concentration va intervenir sur la valeur du potentiel d'équilibre et sur celles des courants observés (lorsque la concentration de H^+ n'est pas trop élevée vis-à-vis de la concentration de la quinone; palier de diffusion proportionnel à la concentration de H^+, en particulier, si $2[H^+[< [Q]$). Une électrode de platine plongeant dans une solution de quinhydrone constitue un système indicateur de concentration des ions H^+(pH), dont l'utilisation pour des titrages potentiométriques à intensité nulle est fort répandue; elle a été également utilisée pour suivre des titrages acides–bases par potentiométrie à intensité constante[46] et par ampérométrie à deux électrodes indicatrices[47]. En présence d'une base, que nous appellerons B, par exemple, une réaction d'oxydation de l'hydroquinone est possible:

$$H_2Q + 2\,B - 2\,e \rightleftharpoons Q + 2\,HB^+$$

Si $2[B] < [H_2Q]$, il apparaît, sur les courbes intensité–potentiel correspondant à l'oxydation de l'hydroquinone, un palier de diffusion de hauteur proportionnelle à la concentration de la base B[44] (Fig. 19). On peut ainsi espérer pouvoir suivre la réaction de cette base B avec une substance quelconque, formation d'un complexe métallique par exemple.

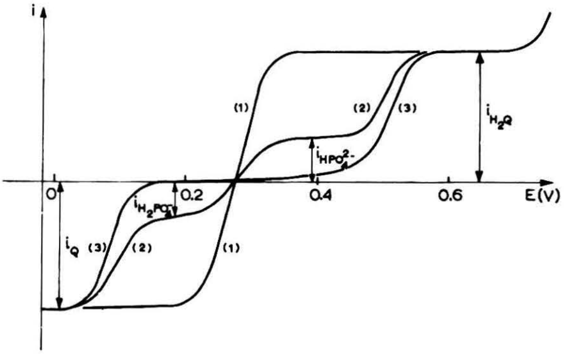


Fig. 19. Courbes $i = f(E)$ expérimentales, à une électrode de mercure, d'oxydation de l'hydroquinone et de réduction de la quinone en présence d'un mélange tampon acide $H_2PO_4^-$/base HPO_4^{2-}. Quinhydrone 0.0012 *M* en présence de tampon phosphate (pH 6.9) 10^{-2} *M* (1), 10^{-3} *M* (2), 10^{-4} *M* et 0 (3). (D'après O. H. MÜLLER[44].)

(D) *Indicateurs polarographiques*

En polarographie classique, on a l'habitude de déterminer des concentrations par mesure de la hauteur du palier de diffusion observé lors de la réduction de substances électroactives. On peut encore imaginer de se servir d'intermédiaires électroactifs, réagissant chimiquement avec des composés non électroactifs, pour déterminer la concentration de ces derniers. Nous appellerons indicateurs polarographiques ces intermédiaires qui permettent ainsi d'étendre le champ des déterminations polarographiques classiques.

Les vagues d'oxydation du mercure d'une électrode à gouttes en présence d'un certain nombre de composés réagissant avec Hg(II) ou Hg(I), Cl^-, Br^-, CN^-, S^{2-}, EDTA, ont une hauteur proportionnelle à la concentration du composé mis en jeu, ce qui permet la détermination de celui-ci[20,21,48,49]. En principe également, le même but peut être atteint avec diverses électrodes métalliques, telles que l'électrode d'argent. Mais des substances solubles peuvent servir d'indicateurs polarographiques.

En 1950, WILLARD ET DEAN[50] ont mis au point une nouvelle méthode de détermination polarographique de l'aluminium à l'aide d'un colorant di-*o*-hydroxy-azoïque, le violet solochrome RS (ou violet pontachrome SW). Ce colorant est réductible à l'électrode à gouttes de mercure et, en présence d'aluminium(III), il donne un complexe stable, plus difficilement réductible. La polarographie d'une solution contenant Al(III) en présence d'un excès de colorant, à un pH convenable, donne donc deux vagues de réduction, dont la seconde, correspondant à la réduction du complexe, est proportionnelle à la concentration de Al(III) et permet sa détermination[51] (Fig. 20).

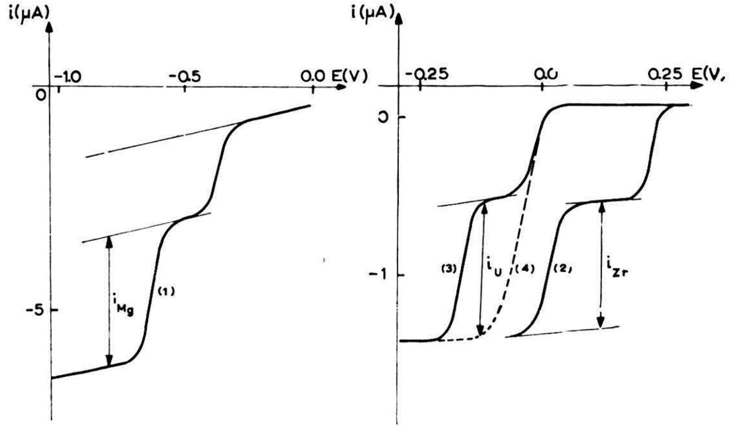


Fig. 20. Colorants azoïques indicateurs polarographiques. (1) Violet solochrome RS en présence de Mg(II). (D'après J. A. DEAN ET H. A. BRYAN[52].) (2) Bleu mordant 2 R en présence de zirconium-(IV) 0.0776 *M*, pH 1.5; (3) Bleu mordant 2 R en présence d'uranium(VI) 0.013 *M*, pH 5.3; (4) Bleu mordant 2 R seul, pH 5.4. (D'après M. ISHIBASHI, T. FUJINAGA ET K. IZUTSU[55].)

Par la suite, le fer(II), le zinc, le magnésium[52], le thorium[53], le zirconium[53], les lanthanides[54] furent déterminés à l'aide du même colorant, l'uranium et le zirconium à l'aide d'un autre colorant du même type, le bleu mordant 2R[55] (Fig. 20).

Remarque: En utilisant la propriété des colorants di-*o*-hydroxyazoïques d'être des indicateurs polarographiques de Al(III), un titrage ampérométrique des ions F^- a été mis au point[56]. On titre F^- par le complexe formé entre Al(III) et le colorant. Ce complexe est moins stable que AlF_6^{3-} et par conséquent, la réaction de titrage est:

$$6\,F^- + \text{Al(III)} - \text{colorant} \rightarrow AlF_6^{3-} + \text{colorant}$$

Nous avons déjà vu que la vague de réduction du colorant précédait celle du complexe Al(III)-colorant. Il suffit de suivre la libération du colorant en imposant à l'électrode de mercure un potentiel compris entre les deux vagues. La hauteur de la vague du colorant croît jusqu'au point équivalent, après lequel elle reste constante, l'excès de complexe n'étant plus détruit (Fig. 21). Sur le même principe, le potassium a été déterminé par mesure de l'abaissement de hauteur de la vague polarographique de la dipicrylamine[57].

On peut encore pousser plus loin l'utilisation des indicateurs polarographiques. Une électrode de mercure est, ainsi que nous l'avons vu, indicatrice de concentration de

TABLEAU I

EXEMPLES D'INDICATEURS ÉLECTROCHIMIQUES

INDICATEURS POLAROGRAPHIQUES

Indicateurs	*Sens de réaction électrochimique indicatrice*	*Exemples de composés dosables*	*Références*
Electrodes métalliques (Hg, Ag, Al . . .)	Oxydation	Hg: Cl^-, Br^-, I^-, CN^-, S^{2-}, EDTA . . . Ag: Cl^-, Br^-, I^-, CN^-, SCN^-, S^{2-} Al: F^-	20, 21, 48, 49 19 22–25
Colorants di-*o*-hydroxyazoïques	Réduction (électrode à gouttes de mercure)	Al(III), Fe(II), lanthanides, Mg(II), Th(IV), U(VI), Zn(II), Zr(IV) Dosage indirect de F^-	52–55 50, 51 56
Dipicrylamine	Réduction (électrode à gouttes de mercure)	K^+	57
Complexe Zn^{2+}–EDTA Complexe Pb^{2+}–EDTA	Réduction de Zn^{2+} et Pb^{2+} libérés (EGM)	Dosage indirect de Ca^{2+} Dosage indirect de Th(IV)	10 58 (voir aussi 59)

INDICATEURS CHRONOAMPÉROMÉTRIQUES

Electrode métallique (Hg)	Oxydation	EDTA Dosage indirect de Ca^{2+}	 17

INDICATEURS AMPÉROMÉTRIQUES (titrages)

Indicateurs		*Electrodes indicatrices*	*Exemples de titrages suivis*	*Références*
Electrodes métalliques (oxydation)	Ag	1 (ou 2 électrodes)	Titrages par halogénures, CN^-, SCN^- (ex.: Ni^{2+} par CN^-, Hg^{2+} par SCN^- . . .)	
	Al	1 électrode	Titrages acides–bases	32
		1 électrode	F^- par Th(IV), Al(III), Ca(II), Mg(II) ou inversement	24, 25
		1 électrode (et 1 de platine)	F^- par Th(IV), Al(III), Ca(II), Mg(II) ou inversement	22, 23
	Hg	1 électrode	Ca^{2+} par l'EDTA	26
Fe^{3+} (réduction)		1 électrode de platine	F^- par Al(III), Ca(II) . . . ou inversement	1–3
Cd^{2+} (réduction)		1 électrode à gouttes de mercure	Ca^{2+} par l'oxalate	3

ZnO_2^{2-} (réduction)	1 électrode à gouttes de mercure	Ca^{2+} par l'EDTA (en présence de Mg^{2+})	9, 10
Colorants di-*o*-hydroxy-azoïques (réduction)	1 électrode à gouttes de mercure	F^- par Al(III)	56
Quinhydrone (benzoquinone + hydroquinone)	2 électrodes de platine	Titrages acides–bases	47
Mercure + complexe Hg^{2+}–EDTA	2 électrodes de mercure (ou Pt, Ag, Au amalgamés)	Ca^{2+}, Zn^{2+} par l'EDTA	11–14
Eau oxygénée, I_2 ou $I^- + IO_3^-$	2 électrodes de platine	Titrages acides–bases	5–7

INDICATEURS POTENTIOMÉTRIQUES (titrages)

Indicateurs	*Electrodes indicatrices*	*Exemples de titrages (ou réactions) suivis*	*Références*
Quinhydrone (benzoquinone + hydroquinone) (et chloranile)	1 électrode de platine ou d'or ($i = 0$) et 2 électrodes de platine ($i = C^{te}$)	Titrages acides–bases	46
$Fe^{3+} + Fe^{2+}$	1 électrode de platine ($i = 0$)	F^- par Pb^{2+} . . . ou inversement	4
Electrode métallique + hydroxyde insoluble (Ag, Al, Hg, Sb, Te, Zr . . .)	1 électrode ($i = 0$)	Titrages acides–bases	Al: 23, 24, 32–35
Electrode d'argent + sel d'argent insoluble (halogénures, CN^-, SCN^- . . .)	1 électrode ($i = 0$) ou 2 électrodes ($i = C^{te}$)	Titrages par Cl^-, Br^-, I^-, CN^-, SCN^-, (ex.: Ni^{2+} par CN^-, Hg^{2+} par SCN^- . . .)	27–29
Electrode de mercure + complexe Hg^{2+}–EDTA	1 électrode ($i = 0$) ou 2 électrodes ($i = C^{te}$)	Ca(II), Ba(II), Sr(II), Zn(II), Cd(II) Cu(II), Bi(III) par l'EDTA	11, 12, 36–41
Electrode de mercure + complexe Hg^{2+}–EDTA + complexe Mg^{2+}–EDTA	1 électrode ($i = 0$)	Réactions de Mg^{2+} (avec oxalate . . .)	42
Electrode de mercure + complexe Hg^{2+}–EDTA + complexe Zn^{2+}–EDTA	1 électrode ($i = 0$)	Réactions de Zn^{2+} (avec citrate)	
Amalgame de plomb + oxalate de plomb + oxalate de calcium	1 électrode (mercure) ($i = 0$)	Réactions de Ca^{2+} (avec citrate . . .)	43
Ferricyanure + ferrocyanure de zinc	1 électrode de platine ($i = 0$)	Réactions de Zn^{2+}	

l'EDTA libre en solution, en raison de la réaction d'oxydation de Hg↓ en HgY et ceci peut être la base d'une détermination polarographique de l'EDTA. Par suite, des cations métalliques irréductibles, formant des complexes stables avec l'EDTA, peuvent être en principe déterminés polarographiquement, par mesure de l'abaissement de la hauteur d'une vague d'oxydation du mercure en présence d'EDTA en excès, après addition de l'échantillon. Malheureusement, les phénomènes sont en général plus compliqués et il apparaît alors des vagues cinétiques qui excluent pratiquement cette possibilité (Fig. 22).

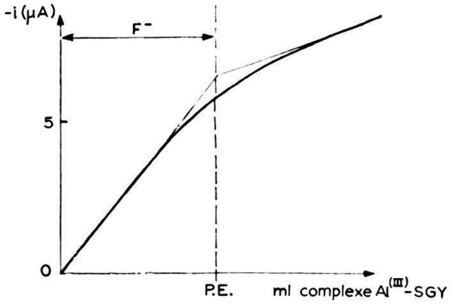


Fig. 21. Titrage ampérométrique de 1.75 mg de F^- par le complexe Al(III)–Superchrome Garnet Y, à pH 4.6. Une électrode indicatrice de mercure, $E = -0.12$ V. (D'après C. R. CASTOR ET J. H. SAYLOR[56].)

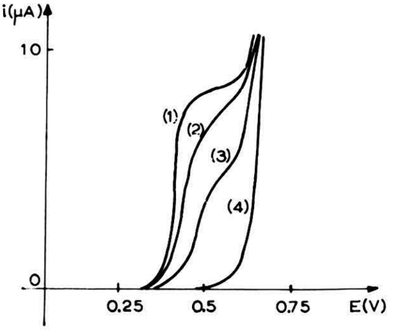


Fig. 22. Oxydation du mercure en présence d'EDTA (1) et de M^{n+} en excès: Mg^{2+} (2), Ca^{2+} (3), Pb^{2+}, Mn^{2+}, Ni^{2+}, Bi^{3+} (4). Electrode à gouttes de mercure. (D'après C. N. REILLEY, W. G. SCRIBNER ET C. TEMPLE[26].)

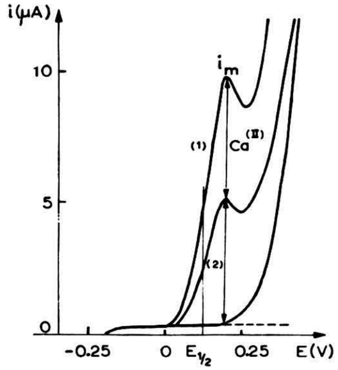


Fig. 23. Détermination de Ca^{2+} par l'EDTA par chronoampérométrie linéaire (vitesse de balayage du potentiel: 1.75 V/min). Electrode de mercure indicatrice. (1) EDTA $2 \cdot 10^{-3}$ *M*, (2) EDTA $2 \cdot 10^{-3}$ *M* + Ca^{2+} 10^{-3} *M*. (D'après M. MORATILLE ET B. TRÉMILLON[17].)

D'autre part, on peut également utiliser une vague de réduction. Si, à une solution du complexe M_1Y en excès (M_1^{2+} étant réductible), on ajoute M_2^{n+} irréductible mais formant un complexe M_2Y plus stable que M_1Y, il y a libération quantitative de M_1^{2+}, dont la vague polarographique de réduction peut être proportionnelle, dans des cas favorables, à la concentration de M_2^{n+} ajouté. De la sorte, ont été réalisés les dosages de Ca^{2+} par déplacement de ZnY en milieu ammoniacal[10], du thorium(IV) par déplacement de PbY[58]. SCHWARZENBACH, GUT ET ANDEREGG[59] ont utilisé aussi cette méthode pour déterminer les constantes de stabilité de différents complexes avec l'EDTA (par déplacement de PbY et CdY) et avec l'acide diamino-1,2 cyclohexane-tétracétique (par déplacement de CuY).

L'oxydation du mercure en présence d'EDTA a pu être encore utilisée pour la détermination des ions Ca^{2+} par chronoampérométrie linéaire[17]. On mesure le courant maximum i_M dû à la diffusion de l'EDTA en excès, avant et après l'addition de l'échantillon de calcium. L'abaissement de i_M permet de déterminer la concentration de Ca^{2+} (Fig. 23).

CONCLUSION

L'ensemble des possibilitées que nous venons d'examiner nous conduit à donner une définition très générale des indicateurs électrochimiques. Un indicateur simple — ou un système indicateur complexe — est un composé — ou un ensemble de composés — électroactif permettant la détermination de corps non électroactifs par une méthode électrochimique d'analyse, polarographie classique, titrages ampérométriques et potentiométriques . . . De façon très générale, on arrive à ce résultat en faisant intervenir le corps à déterminer ou des corps qui réagissent chimiquement avec lui, dans une réaction électrochimique, qui est dite alors réaction indicatrice. Ce principe permet, comme les quelques exemples que nous avons décrits le montrent, d'étendre considérablement le champ d'application des méthodes électrochimiques d'analyses.

RÉSUMÉ

L'introduction des méthodes électrochimiques d'analyse a permis d'envisager des indicateurs de fin de réaction, analogues aux indicateurs colorés. On utilise les propriétés d'électroactivité de ces indicateurs électrochimiques, qui entrent en réaction à la fin du titrage, pour mettre en évidence le point équivalent de celui-ci, par une mesure potentiométrique ou ampérométrique. On peut ainsi titrer: F^- par Al^{3+}, Pb^{2+} ou Th^{4+}, avec Fe^{3+} comme indicateur ampérométrique, ou $Fe^{3+} + Fe^{2+}$ comme indicateur potentiométrique; un acide par une base, avec de l'eau oxygénée ou de l'iode comme indicateur ampérométrique.

La possibilité de tracer la courbe de titrage complète, soit potentiométriquement, soit ampérométriquement, permet de généraliser la notion d'indicateur électrochimique. En premier lieu, la quantité d'indicateur ajouté peut être importante, du même ordre de grandeur que celle du corps titré, pourvu que l'indicateur ne réagisse qu'après celui-ci. La quantité d'indicateur devient ainsi uniquement tributaire de ses conditions d'électroactivité. Si l'on ne peut doser que la somme des quantités de corps en solution y compris l'indicateur lui-même, il suffit de connaître la quantité d'indicateur ajouté, ou de la prédéterminer. Des exemples de titrages utilisant ce procédé sont décrits: dosages d'éléments métalliques non électroactifs par l'EDTA, avec divers éléments électroactifs comme indicateurs.

Plus généralement encore, toute réaction électrochimique mettant en jeu un corps non électroactif mais nécessaire à l'apparition de cette réaction, peut être utilisée pour suivre une réaction de titrage où ce corps intervient. On peut ainsi doser potentiométriquement ou ampérométriquement: divers éléments métalliques, non électroactifs, par l'EDTA, avec électrode indicatrice de mercure, par CN^-, avec électrode

indicatrice d'argent, par F^-, avec électrode indicatrice d'aluminium; un acide par une base, avec électrode indicatrice d'aluminium, d'antimoine. Des systèmes très complexes, tels que platine/quinhydrone pour les titrages acides–bases, mercure/Hg^{2+}–EDTA+ M^{2+}–EDTA pour les dosages de M^{2+}..., peuvent encore être utilisés comme indicateurs électrochimiques.

Enfin, différents composés électroactifs, qui réagissent avec des corps non électroactifs, tels des colorants di-*o*-hydroxy-azoïques avec Al^{3+}, permettent de déterminer ces derniers par un dosage polarographique. Nous pouvons alors considérer ces composés électroactifs comme des indicateurs polarographiques.

Ce principe très général des indicateurs électrochimiques — composés électroactifs permettant la détermination de corps non électroactifs par une méthode électrochimique d'analyse — permet d'étendre considérablement le champ d'action de ces méthodes.

REFERENCES

[1] M. SUNDARESAN ET M. D. KARKHANAVALA, *Current Sci. (India)*, 23 (1954) 258.
[2] A. RINGBOM, *Tek. Kid.*, 77 (1947) 755.
[3] A. RINGBOM ET B. WILKMAN, *Acta Chem. Scand.*, 3 (1949) 22.
[4] L. FARKAS ET N. URI, *Anal. Chem.*, 20 (1948) 237.
[5] D. R. CLIPPINGER ET C. W. FOULK, *Ind. Eng. Chem., Anal. Ed.*, 11 (1939) 216.
[6] H. L. KIES, *Thèse*, Delft (1956); *Anal. Chim. Acta*, 18 (1958) 14.
[7] H. H. WILLARD ET F. FENWICK, *J. Am. Chem. Soc.*, 45 (1923) 715.
[8] G. CHARLOT, J. BADOZ-LAMBLING ET B. TRÉMILLON, *Les Réactions Electrochimiques*, Masson, Paris, 1959.
[9] H. A. LAITINEN ET R. F. SYMPSON, *Anal. Chem.*, 26 (1954) 556.
[10] R. PRIBIL ET E. VICENOVA, *Chem. Listy*, 46 (1952) 535.
[11] G. GUÉRIN, J. DESBARRES ET B. TRÉMILLON, *J. Electroanal. Chem.*, 1 (1960) 226.
[12] C. N. REILLEY ET W. W. PORTERFIELD, *Anal. Chem.*, 28 (1956) 443.
[13] A. E. MARTIN ET C. N. REILLEY, *Anal. Chem.*, 31 (1959) 992.
[14] G. MICHEL, *Anal. Chim. Acta*, 10 (1954) 87.
[15] J. GOFFART, G. MICHEL ET G. DUYCKAERTS, *Anal. Chim. Acta*, 9 (1953) 184.
[16] B. MATYSKA ET I. KÖSSLER, *Collect. Czechoslov. Chem. Communs.*, 16 (1951) 221.
[17] M. MORATILLE ET B. TRÉMILLON, *Bull. soc. chim. France*, (1961) 506.
[18] J. COURSIER, *Thèse*, Masson, Paris, 1954.
[19] J. BADOZ-LAMBLING, *Bull. soc. chim. France*, (1954) 370.
[20] I. M. KOLTHOFF ET C. S. MILLER, *J. Am. Chem. Soc.*, 63 (1941) 1405, 2732.
[21] J. REVENDA, *Collect. Czechoslov. Chem. Communs.*, 6 (1934) 453.
[22] B. B. BAKER ET J. D. MORRISON, *Anal. Chem.*, 27 (1955) 1306.
[23] N. DUMONTIER-GOUREAU ET B. TRÉMILLON, *Bull. soc. chim. France*, (1959) 132.
[24] I. M. KOLTHOFF ET C. J. SAMBUCETTI, *Anal. Chim. Acta*, 21 (1959) 17.
[25] I. M. KOLTHOFF ET C. J. SAMBUCETTI, *Anal. Chim. Acta*, 21 (1959) 233; 22 (1960) 253.
[26] C. N. REILLEY, W. G. SCRIBNER ET C. TEMPLE, *Anal. Chem.*, 28 (1956) 450.
[27] W. BOHNHOLTZER, *Z. anal. Chem.*, 87 (1932) 401.
[28] E. MÜLLER ET H. LAUTERBACH, *Z. anal. Chem.*, 61 (1922) 457.
[29] I. M. KOLTHOFF ET E. J. A. H. VERZYL, *Rec. trav. chim.*, 42 (1923) 1056.
[30] I. M. KOLTHOFF ET C. J. SAMBUCETTI, *J. Am. Chem. Soc.*, 81 (1959) 1516.
[31] I. M. KOLTHOFF, E. J. MEEHAN ET C. J. SAMBUCETTI, *Anal. Chim. Acta*, 22 (1960) 351.
[32] I. M. KOLTHOFF ET C. J. SAMBUCETTI, *Anal. Chim. Acta*, 21 (1959) 155.
[33] I. PRAZAK ET J. GRIMMER, *Collect. Czechoslov. Chem. Communs.*, 24 (1959) 2049.
[34] E. SCARANO, *Anal. Chim. Acta*, 16 (1957) 365; *Gazz. chim. ital.*, 88 (1958) 1195.
[35] E. SCARANO ET S. SIGNORETTI, *J. Electroanal. Chem.*, 1 (1960) 218.
[36] J. S. FRITZ, M. J. RICHARD ET S. K. KARRAKER, *Anal. Chem.*, 30 (1958) 1347.
[37] C. N. REILLEY ET R. W. SCHMID, *Anal. Chem.*, 30 (1958) 947.
[38] C. N. REILLEY, R. W. SCHMID ET D. W. LAMSON, *Anal. Chem.*, 30 (1958) 953.
[39] F. S. SADEK ET C. N. REILLEY, *Microchem. J.*, 1 (1957) 183.
[40] S. SIGGIA, D. EICHLIN ET R. C. RHEINHART, *Anal. Chem.*, 27 (1955) 1745.
[41] F. STRAFELDA ET J. RIHOVA, *Collect. Czechoslov. Chem. Communs.*, 25 (1960) 1444.
[42] G. SCHWARZENBACH ET G. ANDEREGG, *Helv. Chim. Acta*, 40 (1957) 1773.
[43] J. JOSEPH, *J. Biol. Chem.*, 154 (1946) 529.

[44] O. H. Müller et J. P. Baumberger, *Trans. Electrochem. Soc.*, 71 (1937) 181; O. H. Müller, *J. Am. Chem. Soc.*, 62 (1940) 2434.
[45] K. J. Vetter, *Z. Elektrochem.*, 56 (1952) 797.
[46] M. Tegze, *Acta Chim. Acad. Sci. Hung.*, 3 (1953) 391.
[47] G. Mann, *Magyar Kém. Folyóirat*, 61 (1955) 26.
[48] I. M. Kolthoff et J. J. Lingane, *Polarography*, Interscience, New York, 1952.
[49] G. W. C. Milner, *Polarography*, Longmans-Green, Londres, 1957.
[50] H. H. Willard et J. A. Dean, *Anal. Chem.*, 22 (1950) 1264.
[51] M. Perkins et G. F. Reynolds, *Anal. Chim. Acta*, 18 (1958) 616, 625.
[52] J. A. Dean et H. A. Bryan, *Anal. Chim. Acta*, 16 (1957) 87.
[53] R. Patzak et M. R. Zaki, *Mikrochim. Acta*, (1959) 274.
[54] T. M. Florence et L. E. Smythe, *Nature*, 187 (1960) 771.
[55] M. Ishibashi, T. Fujinaga et K. Izutsu, *J. Electroanal. Chem.*, 1 (1959) 26.
[56] C. R. Castor et J. H. Saylor, *Anal. Chem.*, 24 (1952) 1369.
[57] D. Monnier et Z. Besso, *Anal. Chim. Acta*, 7 (1952) 380.
[58] H. Flaschka, S. Khalafalla et F. Sadek, *Z. anal. Chem.*, 156 (1957) 169.
[59] G. Schwarzenbach, R. Gut et G. Anderegg, *Helv. Chim. Acta*, 37 (1954) 937.
[60] D. M. H. Kern, *J. Am. Chem. Soc.*, 81 (1959) 1563.
[61] A. Langer, *Ind. Eng. Chem., Anal. Ed.*, 12 (1940) 511; G. S. Luzina, *Zavodskaya Lab.*, 15 (1949) 1412.

DIFFUSION POLARISATION OF THE HYDROGEN ELECTRODE*

II. EXPERIMENTAL

A. H. M. COSIJN**

Laboratory for Analytical Chemistry, State University, Utrecht (The Netherlands)

(Received November 18th, 1960)

1. INTRODUCTION

In part I of this paper[1] the features of the current-potential curves of the stationary hydrogen electrode in 0.1 *M* KCl, 0.1 *M* K_2SO_4, (1 : 1) acetic acid-sodium acetate and (1 : 1) mono-dihydrogen phosphate solutions have been discussed. The present part deals with the measurements which have been performed at the platinised platinum hydrogen electrode in order to verify the theory.

2. EXPERIMENTAL

(a) *Method of measurement and apparatus*

In the experiments of NAGEL AND WENDLER[2] performed at the hydrogen electrode in unbuffered solutions, the limiting current densities were not proportional to the bulk concentrations of H^+ and OH^- in the pH range 5–9 .This is not surprising since the authors recorded their curves polarographically. Consequently, the rate of change of the potential was too fast to realise steady-state measurements in solutions containing only a few potential determining species. Moreover in these solutions the condition of a non-polarisable reference electrode had not been satisfied because the same platinum electrode was used both as auxiliary and reference electrode. The authors themselves acknowledged this shortcoming.

In the experiments described in this paper the polarisation curves were measured by fixing manually the successive current intensities and measuring the corresponding potentials of the indicator electrode against a saturated calomel electrode. At each current step we waited for a constant potential reading. This discontinuous galvanostatic method enabled us to determine all points on the curves under steady-state conditions. A schematic diagram of the circuit is shown in Fig. 1.

The electrolytic cell E was fed by a power supply PSA whose stabilised output voltage (240–290 V) was large enough to maintain the current intensity at a constant value. By means of the potentiometer ACB (2200 Ω; 0.35 A) and the variable resistance R (0.05–10 MΩ) any desired current through the cell could be obtained by adjustment. The intensity of the current was read on a galvanometer G while the

---

* The work reported in this paper was taken from the Doctorate Thesis of A. H. M. COSIJN, Utrecht, The Netherlands, July, 1959.

** Present address: Central Laboratory, Koninklijke Industrieele Maatschappij v/h Noury & van der Lande N.V., Deventer, The Netherlands.

potential of the indicator electrode against the reference electrode was measured on a tube voltmeter V which could be connected to a recorder.

As the electrolytic cell a modified form of the U-type cell recommended by VETTER[3]

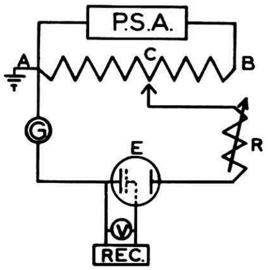


Fig. 1. Circuit.

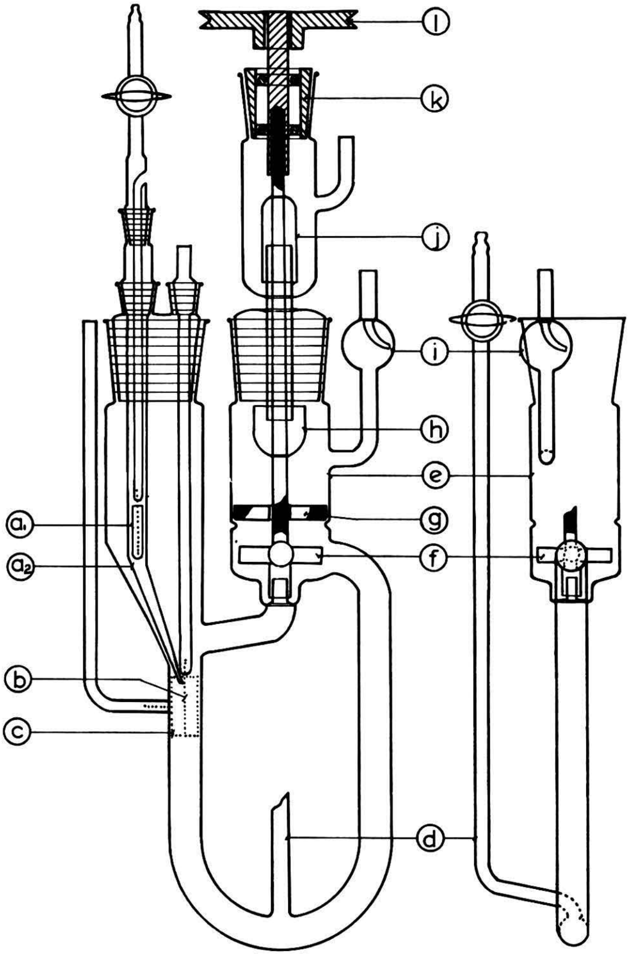


Fig. 2. Electrolytic cell.

was used (Fig. 2)*. In this modified cell the solution moves from right to left by means of a rotating stirrer (f) which acts as a centrifugal pump. Thus a laminar flow along the platinum wire (b) acting as the indicator electrode is realised. This removable electrode is centred in the axis of a cylindric platinum electrode (c) by which arrangement a uniform current intensity across the surface of the indicator electrode is virtually ensured. A saturated calomel reference electrode (a) is brought to near the indicator electrode by way of a Luggin capillary. Gas, if wanted, may enter through the tube (d) and escape *via* the bulb (i).

(b) *Procedure*

The platinum electrodes were platinised as recommended by BATES[4]. Before each experiment the indicator electrode was cleaned and platinised again. Before and during electrolysis a regular stream of purified hydrogen gas was bubbling along the electrode at the rate of 150–160 bubbles/min. Thus reproducible hydrogen electrodes were obtained and the stream of gas consolidated the regularity of the flow of liquid without disturbing the constancy of the current intensity and potential. The stirrer rotated at the rate of 1250 rev/min. The whole cell containing 50 ml of solution was immersed in a thermostat bath at 25° $\pm$ 0.1. For each experiment a freshly prepared solution was used. All chemicals were of A.R. quality. The distilled water was boiled to remove most of the dissolved oxygen before use.

Unbuffered solutions with $pH > 5$ were prepared by the following procedure. A solution of the base electrolyte was acidified to slightly below $pH = 5$ and next boiled to remove traces of carbonate as CO_2. After this the solution was pre-electrolysed in the cell using the cylindric hydrogen electrode as cathode and the calomel electrode as anode. The duration of electrolysis chosen was dependent on the desired value of pH. After termination of the pre-electrolysis the polarised calomel electrode was quickly exchanged for a new one. The determination of the polarisation curve was started when the cell had become acclimatised and the potential of the indicator electrode against the reference electrode had reached a constant value. In unbuffered solutions with $5.5 < pH < 8.5$ the potential of the indicator electrode was found at first, after pre-electrolysis, to increase at a slow rate up to a certain value (2 to 3 h), next to maintain this value for a time and thereafter to decrease still more slowly. In this case the "return value" was assumed to correspond to the pH of the solution and the electrolysis was started at that time.

In most cases in acidic solutions only the cathodic part of the curve and in alkaline solutions only the anodic part of the curve was determined. The experiments were carried out in such a way that the inflexion point of the ionic plateau was reached in 20 to 30 i-steps in the case of unbuffered solutions and in about 15 steps in the case of buffered solutions. At each current intensity we waited till the potential of the indicator electrode had obtained a constant value. Near the inflexion point where the change of potential is greatest, this time of waiting could be more than 1 h. Only in a few cases were the curves also measured backwards whereby some hysteresis was found. All data in the following section are related to rising curves. After termination of the measurement of a curve the electrodes were controlled by verifying the potential at current intensity equal to zero.

---

* The author is much indebted to Dr. J. SLUYTERS who developed the cell.

3. RESULTS

(a) *Current-potential curves in 0.1 M KCl and 0.1 M K_2SO_4 solutions*

As was pointed out in section 3(a) of part I[1], the current-potential relations derived for completely dissociated solutes may be expected to govern the polarisation curves in alkali chloride solutions.

In alkali sulphate solutions, however, these relations will not hold when the medium is acidic or neutral because of the incomplete dissociation of the bisulphate ion. In such solutions the equations which hold for partly dissociated acids will govern the curves (section 3(b), part I).

In order to verify these predictions a number of polarisation curves were measured in 0.1 *M* KCl and 0.1 *M* K_2SO_4 solutions covering the pH range 3–11. The results obtained in these experiments will be discussed below.

(i) *Current density of the inflexion point as a function of pH.* As the position of the inflexion point is the best-defined characteristic for the curves, the experimental values of log $|i_b|$ obtained from two series of measurements are plotted as a function of pH in Figs. 3 and 4.

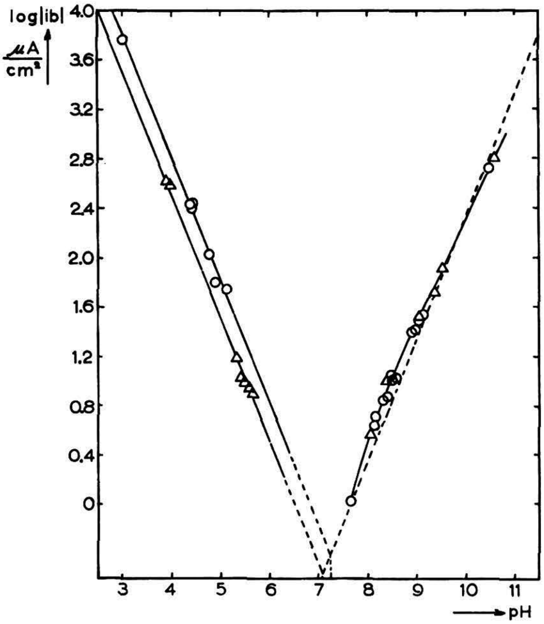


Fig. 3. Log $|i_b|$ as function of pH in unbuffered solutions (series 1): O, experimental values in 0.1 *M* K_2SO_4; △, experimental values in 0.1 *M* KCl; ----, auxiliary line, beyond pH = 8 theoretical line.

One sees that in acidic media the points measured for both chloride and sulphate solutions form a straight line with a slope of $(\Delta \log |i_b|)/(\Delta \text{pH}) = -1$. This is in complete agreement with the theory (part I) as follows from eqns. 23 and 48 in combination with 11 if one considers that the ratio $i_{g\text{HSO}_4}/i_{g\text{H}}$ is virtually constant over the pH range 3–6.5 whereas $i_{g\text{OH}}$ does not influence log $|i_b|$ appreciably until the pH reaches 6.3.

In alkaline media, the points measured should form a straight line with a slope equal to +1. This follows from eqns. 23 and 48 in combination with 12 if one considers that i_{gH} and i_{gHSO_4} do not influence log $|i_b|$ appreciably in solutions with pH > 8. The figures demonstrate that in these cases theory and experiment do not agree fully. A slight curvature of the experimental line is preceptible. The cause of this discrepancy is not known. Theoretically, the straight chloride and sulphate lines in both acidic and alkaline media do not turn off until pH = 6.3 and 8, respectively. From then they decline gradually and approach asymptotically to the vertical lines drawn through the pseudo-neutral points of 0.1 *M* KCl and 0.1 *M* K_2SO_4, respectively, since at the pH values of these points log $|i_b| = -\infty$ (section 2(b)(iii), part I).

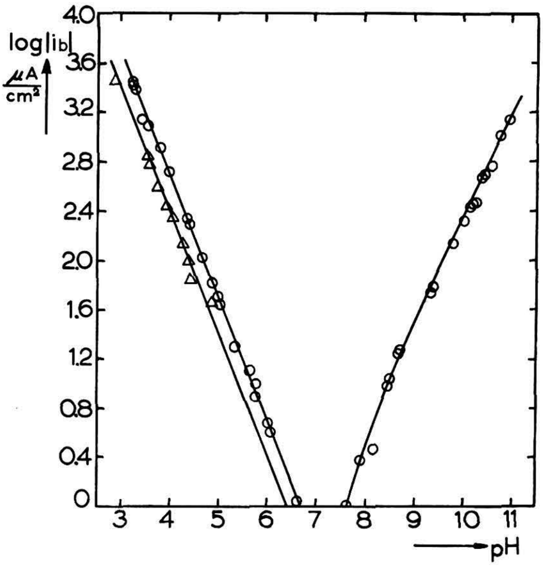


Fig. 4. Log $|i_b|$ as function of pH in unbuffered solutions (series 2): ○, experimental values in 0.1 *M* K_2SO_4; △, experimental values in 0.1 *M* KCl.

(ii) *Current density of the inflexion point dependent on the nature of the base electrolyte.* In the alkaline regions of Figs. 3 and 4 all the points measured are situated on the same line whereas in the acidic regions the chloride and sulphate points form two separate lines at a distance of 0.3 log unity. This is in complete agreement with the theory as will be shown below.

Since i_b is proportional to the concentration whereas pH is determined by the hydrogen ion activity, the values of i_b measured in solutions showing the same value of pH, but containing different supporting electrolytes such as 0.1 *M* KCl and 0.1 *M* K_2SO_4, may differ in consequence of the following factors:

(a) the difference in liquid junction potential at the interfaces sat. KCl–0.1 *M* KCl and sat. KCl–0.1 *M* K_2SO_4;

(b) the difference in the thickness of the diffusion layer as a result of the difference in viscosity and density of 0.1 *M* KCl and 0.1 *M* K_2SO_4, respectively;

(c) the incomplete dissociation of the bisulphate ion;

(d) the difference in equivalent conductance of both H^+ and OH^- in 0.1 M KCl and 0.1 M K_2SO_4, respectively;

(e) the difference in activity coefficient of both H^+ and OH^- ions in these solutions resulting in unequal concentrations at identical values of pH.

Quantitatively these various factors influence the position of the sulphate line with regard to the chloride line in the following way:

(a) At the interface sat. KCl–0.1 M KCl the liquid junction potential is virtually zero[5,6]; at the interface sat. KCl–0.1 M K_2SO_4 it is, at most, a few millivolts different[6]. This means that when using a saturated calomel reference electrode the lines scarcely separate as a result of the unequal liquid junction potentials which are enclosed in the pH determination.

(b) In the electrolytic cell a laminar flow of liquid along the indicator electrode was realised. In such a case one has[7]

$$\delta \approx (\eta/d)^{1/6}$$

where η = viscosity and d = density.

From the literature one can calculate at 25° that

$$\eta(0.1\ M\ \mathrm{KCl})/\eta(0.1\ M\ \mathrm{K_2SO_4}) = 0.977\ ^{8}$$

and

$$d(0.1\ M\ \mathrm{K_2SO_4})/d(0.1\ M\ \mathrm{KCl}) = 1.014\ ^{9}$$

Hence

$$\delta(0.1\ M\ \mathrm{KCl})/\delta(0.1\ M\ \mathrm{K_2SO_4}) = 0.998.$$

This means that, under identical conditions of stirring, the values of i_b in 0.1 M KCl and 0.1 M K_2SO_4 solutions containing equal concentrations of hydrogen or hydroxyl ions, differ by about 2%. This effect is too small, however, to be noticeable in the log $|i_b|$–pH diagrams.

(c) and (d) Taking into account these factors a difference $\Delta \log |i_b|$ is found which has already been discussed in section 3(c) of part I. From the figure shown there it is seen that in acidic media the sulphate line separates 0.1 log-unit from the chloride line, whereas in alkaline media a negligible shift in the opposite direction is found.

(e) In Table II of part I, calculated values of f_H in both solutions are tabulated. Using these values one can calculate that when the values of $p c_H$ are identical, the pH of a 0.1 M K_2SO_4 solution surpasses that of a 0.1 M KCl solution by 0.2 unit. Consequently, the sulphate line in the acidic region of the log $|i_b|$–pH diagram will be shifted 0.2 log-unit upwards with respect to the chloride line.

Considering all the factors, the sulphate line in acidic media can be expected to be situated, theoretically, about 0.3 log-unit above the chloride line. From Figs. 3 and 4 it can be seen that the experimental data are in complete agreement with this prediction*.

The positions of both lines in alkaline media can be found most easily by calculating the position of the pseudo-neutral points of both solutions on the pH axis, next drawing the vertical lines through these points and then determining the points of inter-

---

* Since the activity coefficient in 0.1 M K_2SO_4 could be calculated only by approximation, the tabulated value may be too low and because of this the agreement may be somewhat less satisfactory.

section with the experimental lines in the acidic region. Lines with a slope of $+1$ starting from these points will represent the theoretical lines in alkaline media. As can be seen from Fig. 3 both lines coincide. This figure also shows that in the alkaline region the experimental data for both solutions fully agree with the theory, except for the slight curvature.

(iii) *Thickness of the diffusion layer.* The theoretical position of the lines in Fig. 3 is based on the empirical position of the chloride line in acidic media. A check on the correctness of the latter is possible by calculating the thickness of the diffusion layer from the measured values of i_b and comparing this with published values of δ which have been measured under the same conditions. At pH $= 4$, for instance, one derives from eqns. 27, 11 and 1 of part I the following expression:

$$\delta_{\mathrm{H}} = -\frac{RT}{F}\lambda_{\mathrm{H}} c_{\mathrm{H}} \cdot 10^{-3}/i_b \tag{1}$$

By substituting the known quantities in the right-hand side of this equation one finds $\delta_{\mathrm{H}} = 0.0032$ cm which is in excellent agreement with literature[3].

(iv) *Diffusion coefficient of the hydrogen molecule.* The average value of the limiting current of the hydrogen molecule was found to be $2.4 \cdot 10^{-3}$ A cm^2.

From eqns. 13 and 2 of part I one obtains

$$i_{g\mathrm{H}_2} = \frac{nF}{\delta_{\mathrm{H}_2}} c_{\mathrm{H}_2} \cdot 10^{-3} D_{\mathrm{H}_2} \tag{2}$$

Furthermore δ_{H_2} is given by

$$\delta_{\mathrm{H}_2} = \left(\frac{D_{\mathrm{H}_2}}{D_{\mathrm{H}}}\right)^{1/3} \cdot \delta_{\mathrm{H}} \tag{3}$$

By substituting (3) in (2) and using the following numerical data: $D_{\mathrm{H}} = 8.35 \cdot 10^{-5}$ cm^2 sec^{-1} (part I); $\delta_{\mathrm{H}} = 0.0032$ cm; $c_{\mathrm{H}_2} = 7.68 \cdot 10^{-4}$ mol liter^{-1}[10]; $n = 2$ eq mol^{-1} and $F = 96{,}500$ coulombs one finds

$$D_{\mathrm{H}_2} = 4.2 \cdot 10^{-5}\ \mathrm{cm}^2\ \mathrm{sec}^{-1}$$

which is in accordance with literature[11-13].

(v) *Potential at the inflexion point.* As was pointed out in section 2(b)(ii) of part I, the electrode potential of the inflexion point does not depend on the pH of the solution. For 0.1 *M* KCl solutions one can calculate from eqn. 25 of part I

$$E_b = -0.419\ \mathrm{mV}$$

and for 0.1 *M* K_2SO_4 solutions one obtains from eqn. 49 of part I

$$E_b = -0.428\ \mathrm{mV}.$$

In Table I the average of the experimental values of E_b corresponding to the two series of measurements shown in Figs. 3 and 4 are tabulated.

In sulphate solutions with pH > 8 one observes a slight deviation between the theoretical and experimental values.

(vi) *Total current–potential curves.* Since the experimental values of i_b have been shown to depend correctly on pH, the total curves can be compared with the corre-

TABLE I

E_b AS A FUNCTION OF pH

Solution	*pH*	*Series*	*Number of curves*	$\bar{E}_b$ *(V)*
0.1 *M* KCl	<7	1	7	—0.419
	>8	1	6	—0.415
0.1 *M* K_2SO_4	<7	2	17	—0.433
		1	6	—0.433
	7.5–7.7	1	2	—0.434
	>7.9	2	16	—0.414
		1	11	—0.417

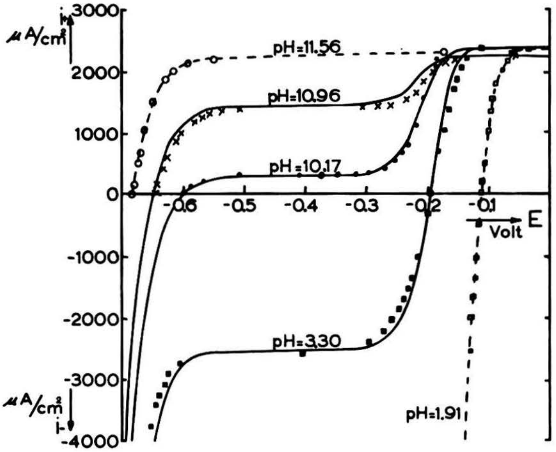


Fig. 5. i–E curves in 0.1 *M* K_2SO_4: ○ × ● □ ■, experimental values; ———, theoretical curves; ----, experimental curves.

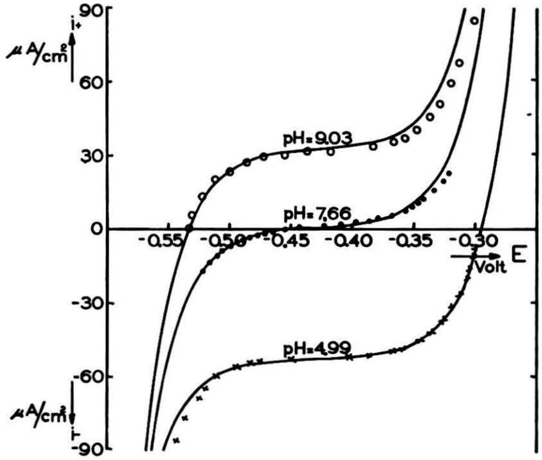


Fig. 6. i–E curves in 0.1 *M* K_2SO_4: ○ ● ×, experimental values; ———, theoretical curves.

sponding theoretical curves by calculating the latter from the general equations of part I using the experimental values for pH, i_b and $i_{g\text{H}_2}$ in combination with the numerical data of Table II, part I. As an illustration some sulphate curves are plotted in Figs. 5 and 6*. The accordance between theory and experiment proves to be very satisfactory.

(b) *Current–potential curves in (1 : 1) acetate buffers*

It has been calculated in section 3(d) of part I that in (1 : 1) acetic acid–sodium acetate buffers only one ionic plateau will occur, *viz.* in the cathodic part of the curve. This has been verified experimentally, as is shown in Fig. 7, where the experimental curves are drawn for two (1 : 1) buffer solutions which contain 10^{-3} *M* and 10^{-4} *M* of both acid and salt, respectively, in addition to 0.1 *M* KCl.

In Table II the experimental values of log $|i_b|$ and η_b at various buffer concentrations are tabulated. A graph of log $|i_b|$ against —log *c* is shown in Fig. 8. As long as $i_{g\text{H}}$ and $i_{g\text{OH}}$ can be neglected with respect to $i_{g\text{HAC}}$ the points ought to be situated on a straight line with the slope —1. This follows from eqn. 44 of part I since the conditions under which this equation holds are fulfilled. Only at the lowest concentration is $i_{g\text{H}}$ not negligible for then $i_{g\text{H}} = 0.65\ i_{g\text{HAC}}$ as can be calculated[14]. This means that the value of log $|i_b|$ increases by 0.22 units.

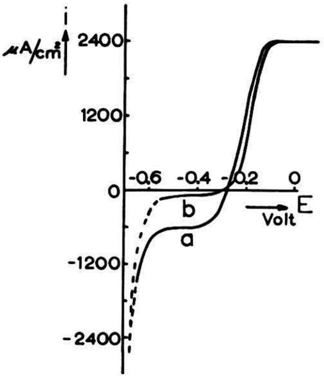


Fig. 7. *i–E* curves of (1 : 1) acetate buffers in 0.1 *M* KCl: a, 10^{-3} *M* HAc + 10^{-3} *M* NaAc; b, 10^{-4} *M* HAc + 10^{-4} *M* NaAc.

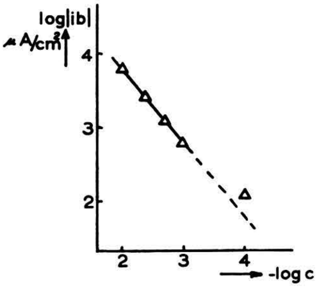


Fig. 8. Log $|i_b|$ as function of —log *c* in (1 : 1) acetate buffers with 0.1 *M* KCl.

It can be seen that the graph is in complete accordance with the theory. In order to check the correctness of the absolute values of i_b, the diffusion coefficient of acetic acid has been calculated using the experimental value of i_b at a concentration above 10^{-3} *M*.

We obtained the value $D_{\text{HAC}} = 1.03 \cdot 10^{-5}$ which is in excellent agreement with literature (see Table II, part I).

The accordance between the experimental and theoretical values of η_b is relatively

---

* More data are given in ref.[14]

satisfactory as may be seen from the last two columns of Table II. At the highest concentration a large difference is observed. This may be a consequence of the fact that in this solution the excess of the supporting electrolyte was not sufficient to suppress the transfer of species by migration.

TABLE II

CATHODIC INFLEXION POINT IN (1 : 1) ACETATE BUFFERS CONTAINING 0.1 M KCl

No.	*Buffer concn. (c)*	*log c*	*pH*	*log* $\lvert i_b \rvert$ *(μA/cm²)*	η_b	η_b *theor.*
1	10^{-2} M	—2	4.65	3.79	—0.311	—0.211
2	$4 \cdot 10^{-3}$ M	—2.4	4.69	3.42	—0.229	—0.198
3	$4 \cdot 10^{-3}$ M	—2.4	4.69	3.43	—0.229	—0.198
4	$4 \cdot 10^{-3}$ M	—2.4	4.70	3.39	—0.229	—0.197
5	$2 \cdot 10^{-3}$ M	—2.7	4.72	3.10	—0.207	—0.187
6	10^{-3} M	—3	4.72	2.82	—0.197	—0.178
7	10^{-4} M	—4	4.86	2.09	—0.164	—0.146
8	10^{-4} M	—4	4.86	2.04	—0.164	—0.146

(c) *Current-potential curves in (1:1) phosphate buffers*

It has been demonstrated in section 3(e) of part I that in (1 : 1) mono-dihydrogen phosphate buffers two ionic plateaus occur, *viz.* one in the cathodic part and the other in the anodic part of the curve.

It can be seen in Fig. 9 that this prediction has been established experimentally.

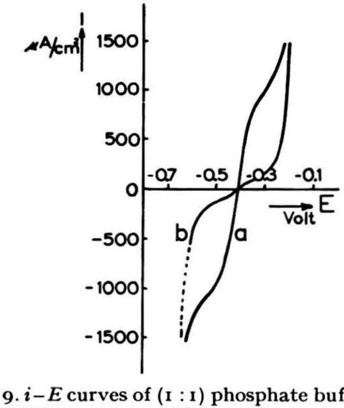


Fig. 9. i–E curves of (1 : 1) phosphate buffers in 0.1 M KCl: a, $2.5 \cdot 10^{-3}$ M KH_2PO_4 + $2.5 \cdot 10^{-3}$ M Na_2HPO_4; b, $2.5 \cdot 10^{-4}$ M KH_2PO_4 + $2.5 \cdot 10^{-4}$ M Na_2HPO_4.

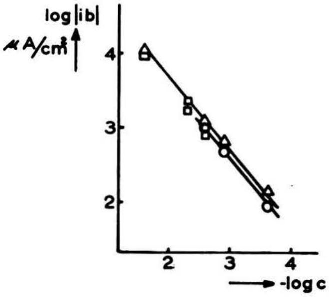


Fig. 10. Log $\lvert i_b \rvert$ as function of —log c in (1 : 1) phosphate buffers: △, cathodic inflexion points in 0.1 M KCl; □, cathodic inflexion points in 0.1 M K_2SO_4; ○, anodic inflexion points in 0.1 M KCl.

In Table III the experimental values of log $\lvert i_b \rvert$ and η_b of both the cathodic and anodic inflexion points in various solutions are tabulated. The graph of log $\lvert i_b \rvert$ against —log c proves to be a straight line with a slope —1, in accordance with eqns. 44 and 45 of part I (Fig. 10). By calculation we found at a concentration of $1.25 \cdot 10^{-3}$ M the following equivalent conductances: $\lambda_{H_2PO_4} = 27$ and $\lambda_{HPO_4} = 21$. In the last column of Table III are given the theoretical values of η_b which have been calculated from eqns. 46 and 47 of part I. The agreement with the experimental values is satisfactory.

At the highest concentration, large differences are observed because of an insufficient excess of the supporting electrolyte.

TABLE III

CATHODIC AND ANODIC INFLEXION POINTS IN (1 : 1) PHOSPHATE BUFFERS CONTAINING 0.1 *M* KCl (Nos. 1–9) OR 0.1 *M* K_2SO_4 (Nos. 10–18)

No.	*Buffer concn. (M)*	*log c*	*pH*	*log* $\lvert i_b \rvert$ *($\mu A/cm^2$)*	η_b	η_b *theor.*
1	$2.5 \cdot 10^{-2}$	—1.6	6.82	4.05	—0.151	
2	$2.5 \cdot 10^{-3}$	—2.6	6.89	3.07	—0.123	—0.130
3	$2.5 \cdot 10^{-3}$, anodic			2.99	+0.115	+0.108
4	$1.25 \cdot 10^{-3}$	—2.9	6.87	2.79	—0.114	—0.122
5	$1.25 \cdot 10^{-3}$, anodic			2.71	+0.106	+0.098
6	$2.5 \cdot 10^{-4}$	—3.6	6.80	2.16	—0.093	—0.105
7	$2.5 \cdot 10^{-4}$, anodic			1.97	+0.086	+0.074
8	$5 \cdot 10^{-3}$ pr.ph. + $2.5 \cdot 10^{-3}$ sec. ph.		6.53	3.37	—0.128	—0.156
9	$5 \cdot 10^{-3}$ pr.ph. + anodic $2.5 \cdot 10^{-3}$ sec. ph.			3.00	+0.120	+0.093
10	$2.5 \cdot 10^{-2}$	—1.6	6.73	4.01	—0.232	—0.159
11	$2.5 \cdot 10^{-2}$	—1.6	6.73	4.01	—0.218	—0.159
12	$5 \cdot 10^{-3}$	—2.3	6.80	3.25	—0.123	—0.135
13	$5 \cdot 10^{-3}$	—2.3	6.77	3.35	—0.148	—0.137
14	$5 \cdot 10^{-3}$	—2.3	6.77	3.35	—0.148	—0.137
15	$2.5 \cdot 10^{-3}$	—2.6	6.79	2.95	—0.145	—0.127
16	$2.5 \cdot 10^{-3}$	—2.6	6.79	3.01	—0.135	—0.127
17	$2.5 \cdot 10^{-3}$	—2.6	6.75	2.93	—0.147	—0.129
18	$2.5 \cdot 10^{-2}$ pr.ph.		4.55	4.04	—0.351	

4. CONCLUSIONS

In unbuffered solutions with $pH < 7$ the theory and experiment are in excellent agreement, particularly with regard to the position of the inflexion point of the curves. In solutions with $pH > 7$ the agreement is somewhat less satisfactory: the relation between log i_b and pH is not entirely linear and the overvoltage at the inflexion point is a little too high in the case of sulphate solutions. In acetate and phosphate buffers the theory and experiment are in complete agreement except for a slight difference between the theoretical and experimental values of the overvoltage at the inflexion points.

In our opinion the results of this investigation justify the following conclusions:

(1) the current-potential curves of the stationary platinised platinum-hydrogen electrode in both unbuffered and buffered solutions are entirely controlled by diffusion polarisation over the pH range investigated, with the exception that in unbuffered solutions with $pH > 7$ slight deviations in the position of the inflexion point appear which require further investigation;

(2) the redox system (H_2, H_2O, H^+, OH^-) behaves reversibly at the platinised platinum-hydrogen electrode under the conditions investigated, even in unbuffered solutions with a pH near 7.

ACKNOWLEDGEMENTS

The author wishes to express his gratitude to Prof. J. SMITTENBERG for his stimulating interest in this investigation. He is much indebted to H. PRINCEN, A. IJZERMANS and P. ZEEGERS who skilfully assisted in the experimental work.

SUMMARY

The present paper deals with the measurement of current-potential curves at the stationary platinised platinum-hydrogen electrode in 0.1 *M* KCl, 0.1 *M* K_2SO_4, (1 : 1) acetic acid-sodium acetate and (1 : 1) mono-dihydrogen phosphate solutions.

The results agree with the theoretical predictions published in part I of the paper.

REFERENCES

[1] A. H. M. COSIJN, *J. Electroanal. Chem.*, 2 (1961) 437.
[2] K. NAGEL AND F. WENDLER, *Z. Elektrochem.*, 60 (1956) 1064.
[3] K. J. VETTER, *Z. physik. Chem.*, (Leipzig), 194 (1950) 199.
[4] R. G. BATES, *Electrometric pH Determinations*, J. Wiley and Sons, Inc., New York, 1954, p. 167.
[5] M. KAHLWEIT, *Z. physik. Chem. (Frankfurt)*, 15 (1958) 196.
[6] R. G. BATES, *Electrometric pH Determinations*, J. Wiley and Sons, Inc., New York, 1954, p. 41.
[7] W. VIELSTICH, *Z. Elektrochem.*, 57 (1953) 646.
[8] M. KAMINSKY, *Z. physik. Chem. (Frankfurt)* 12 (1957) 206.
[9] *International Critical Tables of Numerical Data*, Vol. III, McGraw-Hill Book Co., Inc., New York and London, 1928, p. 87, 88.
[10] A. SEIDELL, *Solubilities of Inorganic and Metal Organic Compounds*, Vol. I, Van Nostrand Co., Inc., New York, 1940, p. 553.
[11] G. HÜFNER, *Z. physik. Chem.*, 27 (1898) 227.
[12] E. AIKASJAN AND A. FEDOROVA, *Doklady Akad. Nauk. U.S.S.R.*, 86 (1952) 1137.
[13] G. TAMMAN AND V. JESSEN, *Z. anorg. allgem. Chem.*, 179 (1929) 125.
[14] A. H. M. COSIJN, *Dissertation*, Utrecht, The Netherlands, 1959.

THE SO-CALLED TENSAMMETRIC WAVES

A. N. FRUMKIN AND B. B. DAMASKIN

Institute of Electrochemistry, Academy of Sciences of the U.S.S.R., Moscow (U.S.S.R.)

(Received January 25th, 1961)

The adsorption of surface-active organic compounds at the mercury/electrolyte interface was first studied by GOUY[1] by the method of measuring the interfacial tension σ. A characteristic electrocapillary curve of a solution containing a surface-active substance (heptyl alcohol) is shown in Fig. 1. As seen from the figure, the organic substance is desorbed from the mercury surface at a sufficiently large positive or negative charge density of the electrode. At the desorption potentials there are sharp changes in the slopes of the electrocapillary curves; these, according to the determination of the differential capacity C and LIPPMAN's equation:

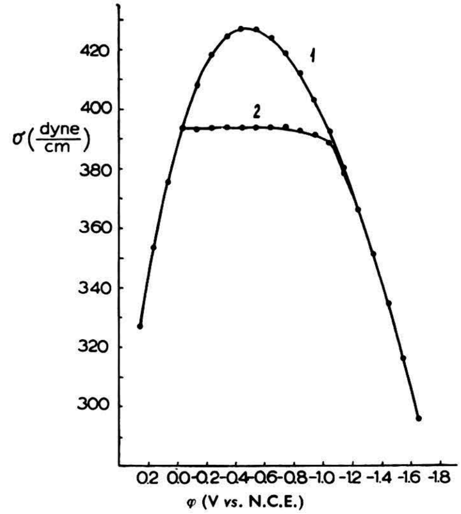


Fig. 1. Electrocapillary curves: (1) 1 N Na_2SO_4; (2) 1 N Na_2SO_4 saturated with n-$C_7H_{15}OH$ (GOUY[1]).

$$C = \frac{d\varepsilon}{d\varphi} = -\frac{d^2\sigma}{d\varphi^2} \qquad (1)$$

correspond to similar changes in the charge density ε over a narrow range of electrode potentials φ and to maxima on the C–φ curves. The interfacial tension itself, however, does not undergo any sharp changes at the desorption potentials, as the decrease in σ due to the adsorption of the organic substance is replaced by a decrease in the interfacial tension due to the ionic adsorption on the charged surface of the electrode.

In the case of strongly adsorbed substances with a carbon chain of sufficient length, the desorption process proceeds like a two-dimensional phase transition[2,3]. In this case, we can speak of a quite definite value of the desorption potential at which the equilibrium between a relatively dense adsorption layer and that corresponding to a very small coverage of the surface is established. Such two-dimensional phase equilibria agree well with the theory of monolayers at the water/air interface[4]. The only difference lies in the fact that at the water/air interface the role of an independent variable, the change of which determines the transition of the surface from one state to another, is played by the surface pressure or the temperature, whereas in the case under consideration such a variable is the potential difference between the electrode and the solution. It is evident that in the course of a two-dimensional phase transition the interfacial tension does not suffer any changes, since the equality of surface pressures of the two surface phases is the condition for equilibrium in the surface layer. In the case of substances with smaller chain lengths the desorption process does not proceed stepwise, but, instead, gradually, so that, to be precise, one should speak of a range of potentials over which the desorption occurs rather than of a desorption potential. In many cases, however, this range is very narrow. The value σ changes somewhat over it, but in a lesser degree than it would over the same range of potentials in the absence of a surface-active substance.

A quantitative theory of the effect of the electric field upon the adsorption of neutral molecules, with the complete equation of the state of the surface layer taken into consideration, has been developed by FRUMKIN[5]. This theory explains why the desorption of adsorbed molecules must proceed over a narrow range of potentials. It follows also from this theory, that when the values of the double-layer capacity are constant in the absence of an adsorbed substance ($C_{\theta=0}$ = const.), as well as at a coverage θ approaching unity ($C_{\theta=1}$ = const.), the desorption potentials φ_d are connected with the concentration of the adsorbed substance c by the equation:

$$\left| \varphi_d \left(\varphi_d \frac{C_{\theta=0} - C_{\theta=1}}{2} + C_{\theta=1}\varphi_N \right) \right| = k_1 + k_2 \ln c \qquad (2)$$

where k_1 and k_2 are constants and φ_N is the shift in the zero charge point upon coverage of the surface by the adsorbed organic substance. Eqn. 2 is in good agreement with the experimental data[3], but is applicable only at such concentrations of the surface-active substance that the adsorption limit is practically attained. The problem of the relationship between the desorption potential and the concentration over a wider range of concentrations and, in particular, that of the limits of applicability of the linear relationship between the desorption potential and the log of the concentration of the substance being adsorbed, which was pointed out in the literature[6,7], will be considered in another paper. FRUMKIN's theory was further developed by HANSEN, MINTURN AND HICKSON[8], who took into consideration the dependence of the double-layer capacity on the electrode potential.

The peaks on the curves of the differential capacity of the double-layer at the desorption potentials of organic substances were first observed by PROSKURNIN AND FRUMKIN[9]. The $C-\varphi$ curve of a solution containing *n*-octyl alcohol measured by these authors is shown in Fig. 2. In this work the values of the double-layer capacity were determined by the method of comparison with a standard capacity C_1. This method consists in measuring at a constant a.c. strength, $\widetilde{\Delta i}$, the voltage drops over the cell, $\Delta\varphi_x$, and over a standard capacity, $\Delta\varphi_1$; the double-layer capacity required can be equated with the quantity:

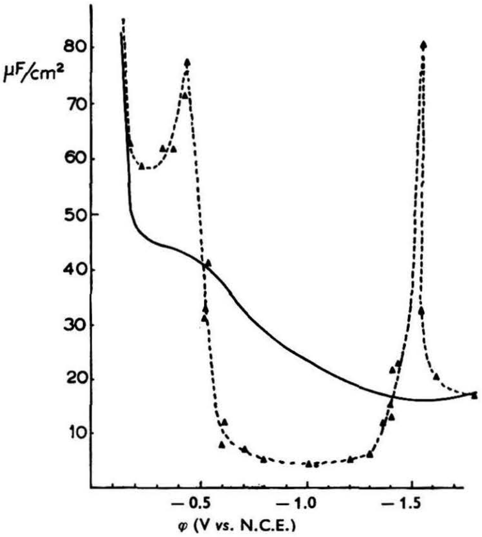


Fig. 2. Differential capacity–voltage curves measured by the method of comparison with a a standard capacity; frequency 50 cycles. Solid curve, *N* Na_2SO_4; broken curve, *N* Na_2SO_4 saturated with $C_8H_{17}OH$ (PROSKURNIN AND FRUMKIN[9]).

$$C_{obs.} = C_1\frac{\Delta\varphi_1}{\Delta\varphi_x} = C_1\frac{\widetilde{\Delta i}\,\dfrac{1}{C_1\omega}}{\widetilde{\Delta i}\sqrt{R_x^2+\dfrac{1}{C_x^2\omega^2}}} = \frac{C_x}{\sqrt{R_x^2C_x^2\omega^2+1}} \tag{3}$$

where R_x and C_x are the ohmic and capacity components of the total impedance of the cell, provided they are connected in series. If no electrochemical reaction occurs on the electrode, R_x corresponds to the resistance of the solution and C_x to the differential capacity of the double layer. From eqn. 3 it is evident that in the case of an ideally polarized electrode the measured value, $C_{obs.}$, can be equated with the double-layer capacity C_x only at a low a.c. frequency and with small resistance of the solution R_x, when the following inequality is fulfilled:

$$R_x^2C_x^2\omega^2 \ll 1 \tag{4}$$

The drawback of this method of comparison which consists in the necessity of satisfying condition (4) was later eliminated by DOLIN AND ERSHLER[10] by using a bridge arrangement providing for separate compensation of the capacity and ohmic components. The bridge method as applied to the case of a dropping electrode was first developed by GRAHAME[11].

In 1952 BREYER AND HACOBIAN[7] proposed a method for the study of the adsorption of surface-active organic compounds at the electrode/solution interface called by these authors "tensammetry" (from the words "surface tension" and "ammetry")[12]. Later this term was widely used in polarographic literature (see reviews)[12,13]. The method consists of measuring the a.c. flowing through a cell $\widetilde{\Delta i}$ depending on the electrode potential which is varied in accordance with the technique generally used in polarography. Since in the general case the impedance of the electrochemical cell can be represented as a resistance R_x and a capacity C_x connected in series,

$$\widetilde{\Delta i} = \frac{\Delta\varphi}{\sqrt{R_x^2 + \frac{1}{C_x^2\omega^2}}} = \Delta\varphi\omega\frac{C_x}{\sqrt{R_x^2 C_x^2\omega^2 + 1}} \tag{5}$$

If no electrode process with a reversible step occurs on the electrode surface, the value of C_x is equal to the double-layer capacity and the resulting $\widetilde{\Delta i}$–φ curve is similar in its shape to the C–φ curve. By comparing eqns. 3 and 4 we see that the "tensammetric" method yields, in principle, the same results as the comparison method, *i.e.* it yields a value proportional to the differential capacity of the double layer if conditon (4) is fulfilled.

In the paper by BREYER AND HACOBIAN[7] the maxima on the $\widetilde{\Delta i}$–φ curves (the so-called "tensammetric waves") are explained, by analogy with a.c. polarography[14], to be due to periodic shifts of the charges in the a.c. field. However, the charges located on the ends of dipoles of adsorbed molecules are considered, rather than the free charges forming part of the double layer. The "tensammetric waves" are supposed to be a result of the periodical reversal of dipoles of the adsorbed substances which are on a high energy level.

It should be pointed out that the term "tensammetric waves" as applied to the desorption peaks on the curves appears unsuitable, since, as has already been noted at the beginning of this paper, there is no characteristic change in the interfacial tension corresponding to the desorption potentials. Moreover, in a number of cases the desorption of a surface-active substance from the electrode surface proceeds stepwise, and at the desorption potential there is a vertical line on the C–φ curve (Fig. 3) to which the term "wave" is obviously inapplicable. In our opinion, it would be more correct, in distinction to a.c. polarograms, to call the $\widetilde{\Delta i}$–φ curves obtained in the case of the adsorption of organic substances, curves of nonfaradaic admittance, whereas the maxima on these curves at the desorption potentials should be called adsorption–desorption peaks or maxima.

As has been shown above, the peaks on the differential capacity curves, as well as on the Δi–φ curves, observed at the desorption potentials of organic substances in the case of low a.c. frequencies result from the shape of the electrocapillary curves in accordance with thermodynamical relationships, and, consequently, their height and shape are fully determined by the dependence of the adsorption of the organic substance on the potential and by its effect on the double-layer capacity*.

The height of the capacity peak, however, varies considerably with the a.c. frequency (see Fig. 4), so that the behaviour of the electrode in the a.c. field should be examined in more detail.

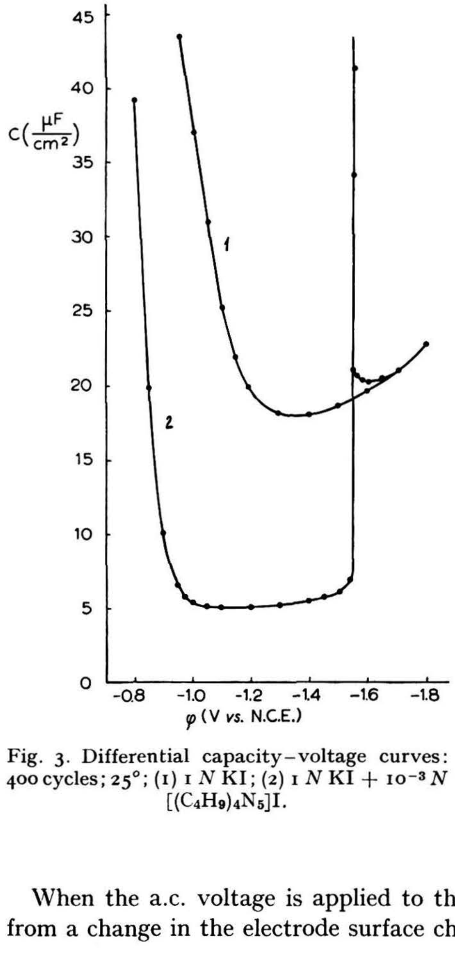


Fig. 3. Differential capacity–voltage curves: 400 cycles; 25°; (1) 1 N KI; (2) 1 N KI + 10^{-3} N $[(C_4H_9)_4N_5]I$.

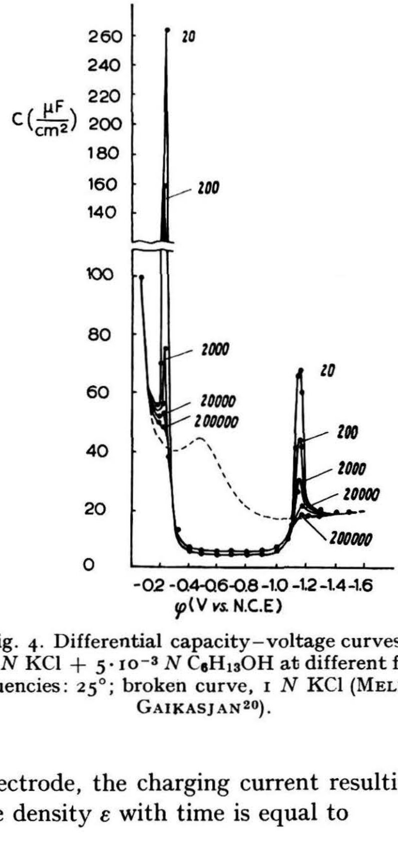


Fig. 4. Differential capacity–voltage curves in 1 N KCl + $5 \cdot 10^{-3}$ N $C_6H_{13}OH$ at different frequencies: 25°; broken curve, 1 N KCl (MELIK-GAIKASJAN[20]).

When the a.c. voltage is applied to the electrode, the charging current resulting from a change in the electrode surface charge density ε with time is equal to

$$i = \frac{d\varepsilon}{dt} \tag{6}$$

---

* The hypothesis has been advanced that the "electro-capillaryphoretic effect", *i.e.* the tangential motion of mercury due to adsorption/desorption processes, exerts a considerable influence upon the peaks on the $\widetilde{\Delta i}-\varphi$ (or $C-\varphi$) curves[15,13]. As has been shown in our laboratory, however, the values of the differential capacity measured by the bridge method in thoroughly cleaned and deoxygenated KCl solutions do not depend on stirring. Consequently, the tangential motion of mercury cannot result in an appreciable increase in the capacity measured. On the other hand, at the desorption potentials of organic substances the capacity peaks are known to be sharply defined in the case of solid electrodes[16–18] as well, where there is no surface motion.

If there is a surface-active organic substance in the solution, the charge density of the electrode surface is a function of the electrode potential φ and of the amount of the surface-active substance adsorbed Γ, *i.e.* $\varepsilon = f(\varphi,\Gamma)$. Therefore

$$i = \frac{\mathrm{d}\varepsilon}{\mathrm{d}t} = \left(\frac{\delta\varepsilon}{\delta\varphi}\right)_{\Gamma} \frac{\mathrm{d}\varphi}{\mathrm{d}t} + \left(\frac{\delta\varepsilon}{\delta\Gamma}\right)_{\varphi} \frac{\mathrm{d}\Gamma}{\mathrm{d}t} = C_e \frac{\mathrm{d}\varphi}{\mathrm{d}t} + i' \tag{7}$$

where C_e is the so-called "true capacity" of the double layer at a constant quantity of the substance being adsorbed (Γ = const) and

$$i' = \left(\frac{\delta\varepsilon}{\delta\Gamma}\right)_{\varphi} \frac{\mathrm{d}\Gamma}{\mathrm{d}t}$$

is the additional charging current density due to the change in adsorption with time.

When the oscillations are of a sinusoidal shape and the equivalent electric scheme shown in Fig. 5 is chosen, the value i' can be written as:

$$i' = \Delta\varphi'\left(\frac{1}{R_i}\cos\omega t - C_i\omega\sin\omega t\right) \tag{8}$$

where C_i and R_i are the additional capacity and additional resistance due to the adsorption/desorption process. As has been shown by FRUMKIN AND MELIK-GAIKASJAN[19],

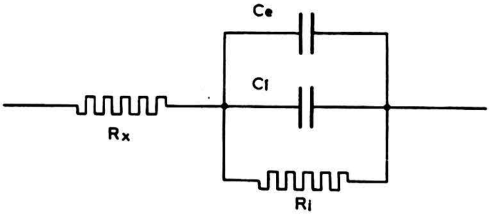


Fig. 5. The equivalent electric scheme of a cell in the case of an adsorption/desorption process occurring on the electrode.

when the rate of the adsorption process is determined by the diffusion step

$$C_i = C_0 \frac{\alpha\omega^{1/2} + 2}{(\alpha\omega^{1/2} + 1)^2 + 1} \tag{9}$$

and

$$R_i = \frac{1}{C_0} \frac{(\alpha\omega^{1/2} + 1)^2 + 1}{\alpha\omega^{3/2}} \tag{10}$$

where C_0 is the value of C_i at $\omega = 0$ and

$$\alpha = \sqrt{\frac{2}{D}}\left(\frac{\partial\Gamma}{\partial c}\right)_{\varphi}$$

D being the diffusion coefficient.

The values of C_i and R_i can be readily determined by means of bridge measurements (but not from $\widetilde{\Delta i}$-φ curves), and from their dependence on the a.c. frequency, conclusions concerning the kinetics of adsorption of surface-active organic substances can be drawn[19-22]. Thus, it has been shown[19-20] that the dependence of C_i on the frequency can be well expressed by eqn. 9 and, consequently, the slowest step in the process of adsorption of a number of organic substances is that of diffusion of the molecules being adsorbed towards the electrode surface. The considerable decrease in the height of capacity peaks with an increase in the frequency (Fig. 4) in this case is due mainly to diffusion difficulties, although according to LORENZ AND MÖCKEL[22], the step due to the real adsorption, proceeding at a large but still finite rate, can also exert an influence upon the dependence of the height of capacity peaks on the a.c. frequency.

It should be noted that in a number of cases peaks are observed on the differential capacity curves, which are not connected with adsorption/desorption processes, but which are caused by changes in the structure of the double layer, in particular, by changes in the orientation of adsorbed particles. As an example the C-φ curve measured in 0.01 N Na_2SO_4 + 10^{-3} N $C_{12}H_{25}OSO_3Na$ solution is shown in Fig. 6[23]. The right-hand side capacity peak is due to the process of desorption of the $C_{12}H_{25}OSO_3^-$ anion from the mercury surface and the dependence of C_i on ω for this peak corresponds to eqn. 9. In contrast, the left-hand side capacity peak on the C-φ curve shown in Fig. 6 is not a desorption peak and the dependence of the height of this peak on the a.c. frequency cannot be expressed by eqn. 9. This dependence is much less sharply expressed, which points to a larger rate for the process. As has been shown[23], the most likely cause of the appearance of this capacity peak is the reorientation of

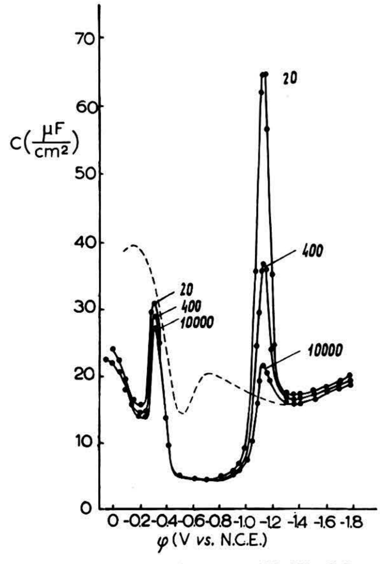


Fig. 6. Differential capacity–voltage curves in 0.01 N Na_2SO_4 + 10^{-3} N $C_{12}H_{25}OSO_3Na$ at different frequencies: 25°; broken curve, 0.01 N Na_2SO_4 (DAMASKIN, NIKOLAEVA-FEDOROVICH AND IVANOVA[23]).

adsorbed particles on the electrode surface with the formation of a micellar film. Similar maxima on the $C-\varphi$ curves not connected with the process of adsorption/desorption have been observed in a number of other investigations[24-26].

Although in the case in question, in contrast to that examined previously, the appearance of the capacity maxima can be due to a change in the orientation of adsorbed particles, BREYER AND HACOBIAN's theory[7] is still not applicable. Irrespective of the nature of the phenomenon occurring in the surface layer at a given potential, the charging current and the differential capacity measured are always determined by the change in the electronic charge density of the mercury surface which is a function of the electrode potential and of the amount of the surface-active substance adsorbed $\varepsilon = f(\varphi,\Gamma)$. In BREYER AND HACOBIAN's theory[7], however, the adsorbed dipoles of the organic substance are considered as "active" charges and the double-layer capacity measured is supposed to be determined by a change in these charges with a change in the electrode potential. In reality, although the electric field acts upon the dipole with a definite force, the total charge of the dipoles of a neutral substance, being always equal to zero, cannot bear a direct relation to the charging current.

It is of interest to compare eqn. 9 of the present paper with eqn. 54 of ref.[7], which gives an expression for the value of the additional ("tensammetric") capacity on the basis of BREYER AND HACOBIAN's theory. As seen from eqn. 9, at $\omega \rightarrow 0$, $C_i = C_0$ and the double-layer capacity measured approaches its equilibrium value $C_e + C_0$. At the same time, according to eqn. (54) of ref.[7] deduced by analogy with the expression for the polarization capacity of an electrochemical process limited by the diffusion rate, at $\omega \rightarrow 0$ $C_i \rightarrow \infty$. In the case of an adsorption/desorption process this result is devoid of physical sense, since at potentials lying beyond the adsorption region, the electrode charge density equal to

$$\varepsilon = \int_{\varphi\ (\varepsilon-0)}^{\varphi} (C_e + C_{i(w \rightarrow 0)})\, \mathrm{d}\varphi$$

has a finite, determinate value*. Thus, the application of relations deduced for the faradaic current to the adsorption/desorption process leads to erroneous results. For the same reason, the data on the kinetics of adsorption of organic compounds obtained by BREYER AND HACOBIAN[27] by means of a method developed earlier for the determination of the rates of electrochemical reactions[28] cannot be considered to be correct. Moreover, as was shown later by BAUER AND ELVING[29], the method described[28] cannot yield correct values of the rate constant for electrochemical reactions, since the results depend, to a very great extent, on the phase angle between the faradaic and the charging currents as well as on the value of the series resistance R_x. In this connection, it proved necessary, in order to study the kinetics of electrochemical processes as well as to measure the double-layer capacity[30], to supplement the measurements of the a.c. value with measurements of the phase angle[31], this being in principle equivalent to the bridge method.

---

* An infinite capacity is theoretically possible in the case of a two-dimensional phase transition at a certain definite value of the potential, but not within some ranges of potentials.

SUMMARY

The term "tensammetry" introduced by BREYER AND HACOBIAN as well as the mechanism proposed by them to explain the appearance of peaks on the differential capacity–voltage curves in the presence of surface-active substance have been critically discussed. The value obtained by the method developed by these authors has been shown to be identical to that determined by the comparison method used by PROSKURNIN AND FRUMKIN. The advantages of the bridge arrangement for the determination of the differential capacity of the electrode have been considered. Curves for the dependence of the differential capacity on the potential are given for the case when the desorption process is that of a two-dimensional phase transition and for that when, at some potentials there occurs a change in the structure of the adsorption layer unaccompanied by its desorption.

REFERENCES

1 G. GOUY, *Ann. chim. et phys.*, [7] 29 (1903) 145; [8] 8 (1906) 291; [8] 9 (1906) 75.
2 A. N. FRUMKIN, *Proc. 2nd Intern. Congr. Surface Activity Electrical Phenomena, 1957*, p. 5.
3 A. N. FRUMKIN AND B. B. DAMASKIN, *Doklady Akad. Nauk S.S.S.R.*, 129 (1952) 862.
4 N. ADAM, *The Physics and Chemistry of Surfaces*, 3d edn., Oxford Univ. Press, London, 1941.
5 A. N. FRUMKIN, *Z. Physik.*, 35 (1926) 792.
6 K. S. G. DOSS AND A. KALYANASUNDARAM, *Current Sci. (India)*, 20 (1951) 199.
7 B. BREYER AND S. HACOBIAN, *Australian J. Sci. Research*, A5 (1952) 500.
8 R. S. HANSEN, R. E. MINTURN AND D. A. HICKSON, *J. Phys. Chem.*, 60 (1956) 1185; 61 (1957) 953.
9 M. PROSKURNIN AND A. FRUMKIN, *Trans. Faraday Soc.*, 31 (1935) 110.
10 P. I. DOLIN AND B. V. ERSHLER, *J. Phys. Chem. (U.S.S.R.)*, 14 (1940) 886.
11 D. C. GRAHAME, *J. Am. Chem. Soc.*, 63 (1941) 1207.
12 H. H. BAUER, *J. Electroanal. Chem.*, 1 (1960) 369.
13 K. S. G. DOSS, *Bull. India Sect. Electrochem. Soc.*, 8 (1959) 84.
14 B. BREYER AND S. HACOBIAN, *Australian J. Chem.*, 7 (1954) 225.
15 K. S. G. DOSS AND V. K. VENKATESAN, *Proc. Indian Acad. Sci.*, 49A (1959) 129.
16 T. I. BORISOVA, B. V. ERSHLER AND A. N. FRUMKIN, *Zhur. Fiz. Khim.*, 22 (1948) 925; 24 (1950) 337.
17 D. I. LEIKIS, *Doklady Akad. Nauk S.S.S.R.*, 135 (1960) 1429.
18 V. L. CHEIFETZ AND B. S. KRASIKOV, *Doklady Akad. Nauk S.S.S.R.*, 94 (1954) 101, 517.
19 A. N. FRUMKIN AND V. I. MELIK-GAIKASJAN, *Doklady Akad. Nauk S.S.S.R.*, 77 (1951) 855.
20 V. I. MELIK-GAIKASJAN, *Zhur. Fiz. Khim. (U.S.S.R.)*, 26 (1952) 560.
21 T. BERZINS AND P. DELAHAY, *J. Phys. Chem.*, 59 (1955) 906.
22 W. LORENZ AND F. MÖCKEL, *Z. Elektrochem.*, 60 (1956) 507, 939.
23 B. B. DAMASKIN, N. V. NIKOLAEVA-FEDOROVICH AND R. V. IVANOVA, *Zhur. Fiz. Khim.*, 34 (1960) 894.
24 J. W. LOVELAND AND P. J. ELVING, *J. Phys. Chem.*, 56 (1952) 935.
25 S. L. GUPTA, *Proc. Indian Acad. Sci.*, 47A (1958) 254.
26 K. EDA, *J. Chem. Soc. Japan*, 80 (1959) 343.
27 B. BREYER AND S. HACOBIAN, *Australian J. Chem.*, 9 (1956) 7.
28 B. BREYER, H. H. BAUER AND S. HACOBIAN, *Australian J. Chem.*, 8 (1955) 322.
29 H. H. BAUER AND P. J. ELVING, *Australian J. Chem.*, 12 (1959) 335.
30 H. H. BAUER AND P. J. ELVING, *Australian J. Chem.*, 12 (1959) 343.
31 H. H. BAUER AND P. J. ELVING, *J. Am. Chem. Soc.*, 82 (1960) 2091.

Remarks on the paper "The so-called tensammetric waves" by A. N. Frumkin and B. B. Damaskin

1. The term "tensammetry" was proposed to describe alternating-current/direct-voltage curves obtained with the dropping mercury electrode in the presence of surfactants, *i.e.* substances which, over a wide range of potentials lower the surface tension at the electrode/solution interface[1]. The term was not intended to describe specifically the changes in interfacial tension during desorption, as the authors imply. We also believe that the expression "tensammetric waves" is preferable to the rather unwieldy term "curves of nonfaradaic admittance" proposed by them.

2. With regard to the theoretical treatment, the authors prefer to look at the process from the point of view of the double-layer ions, whereas we considered it from the point of view of the dipole molecules undergoing the adsorption/desorption process; which of the two points of view is preferable, only time can show.

It seems, however, rather regrettable that the authors have chosen to disregard the effect of a highly non-uniform field on the dipole molecules contained in it; by consequence, they have completely misunderstood our concept of "active charges". We have, of course, never claimed that these carry a net free charge, as the authors seem to imply; we have clearly satted (p. 501) that in a non-uniform electric field "the dipole will behave *as if* it were a charged particle".

3. With regard to our method[2] for the investigation of the rate of electrode processes, once again we never claimed, as the authors imply, that it can yield "correct values of the rate constant"; on the contrary, we have repeatedly stated, in the paper quoted by them, that the results have relative significance only.

Finally, we should like to say that we feel highly gratified that the different physical pictures lead to one and the same conclusion, *viz.* that the capacity peaks are a linear function of the logarithm of the bulk concentration of surfactant (*cf.* eqn. 2 in the paper by FRUMKIN AND DAMASKIN, and eqn. 38 in our paper[1]).

4. With regard to eqn. 54, we agree that it should be revised in the light both of our later work on electrode processes in alternating fields[3], and of the results of phase angle measurements, so far unpublished.

Institute of Agricultural Chemistry,
University of Sydney (Australia)

B. BREYER AND
S. HACOBIAN

---

[1] B. BREYER AND S. HACOBIAN, *Australian J. Sci. Research*, A5 (1952) 500.
[2] B. BREYER, H. H. BAUER AND S. HACOBIAN, *Australian J. Chem.*, 8 (1955) 322.
[3] B. BREYER AND S. HACOBIAN, *Australian J. Chem.*, 7 (1954) 225.

Received March 14th, 1961

ELECTROGENERATION OF BROMINE BY A PULSE TECHNIQUE FOR COULOMETRIC TITRATIONS

QUINTUS FERNANDO, M. A. V. DEVANATHAN*, J. C. RASIAH,
J. A. CALPIN** AND K. NAKULESPARAN***

Dept. of Chemistry, University of Pittsburgh, Pittsburgh, Pa. (U.S.A.)

(Received February 3rd, 1961)

INTRODUCTION

A coulometric technique using pulses of constant magnitude has been described by DEVANATHAN AND FERNANDO[1]. In the instrument that they described, pulses of constant magnitude were generated with the aid of a multivibrator and electromechanically counted. A constant pulse size was achieved by using a high stability power supply of relatively complex design. It was considered useful to investigate the performance of this instrument when the power supply was replaced with a simplified or a readily obtainable power pack. Two such power supplies have been used in this work, a conventional power pack regulated with "Barretter tubes", and a Healthkit Model PS-3 power supply. The constancy of the current pulses generated by this simplified multivibrator has been tested directly by means of a silver as well as a copper coulometer, and indirectly by titrating arsenic(III) and 8-quinolinol with electrogenerated bromine.

The indicator circuit has also been studied in order to determine the optimum conditions for the amperometric detection of the end-point in bromometric titrations.

EXPERIMENTAL

Coulometric titrations with electrogenerated bromine

Fig. 1 shows the multivibrator circuit used. A Healthkit Model PS-3 "Variable Voltage Regulated Power Supply" served as the source of anode voltage. Steady anode voltages were obtained about 15 min after switching this device on. Switches S_1 and S_2 permitted the selection of one of three resistances, 100 KΩ, 500 KΩ and 1 MΩ as the grid bias of the tubes V_1 and V_2. Consequently nine combinations of R_1 and R_2 were possible, seven of which were found to allow the generation of pulses at a steady rate when $B+$ was 250 V. If $B+ = 200$ V it was found that all combinations of R_1 and R_2 gave pulses at a steady rate (Table I). The magnitude as well as the rate of generation of the current pulses are critically dependent on the anode voltage and the values of C_1, C_2, R_1 and R_2. Switch S_3 was used to short circuit the cathode of V_2 to ground so as to permit the multivibrator to run freely when not connected to the titration cell. A high speed relay, which operated an electric counter, was

---

* Present address: Dept. of Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania.

** Present address: Rohm and Haas Company, Philadelphia, Pennsylvania.

*** Present address: Shell Company of Ceylon, Ltd., Colombo, Ceylon.

connected on the anode line of V_2 and the titration cell was connected between the cathode of V_2 and earth.

The titration cell consisted of a central flat-bottomed vessel in which the generator cathode and a platinum indicator electrode were placed. Two side arms were fused on either side of the central vessel; these were saturated calomel reference electrodes and were separated from the central compartment by sintered discs and agar plugs. One of the reference electrodes and the platinum generator cathode were connected to *E* and *K* respectively in the multivibrator circuit shown in Fig. 1. The second reference electrode and a platinum electrode of area 5.38 cm² were used as the indicator electrodes. A platinum microelectrode, rotated at a speed of about 600 rev/min with a Sargent synchronous motor was also used as an indicator electrode and proved to be far superior to the platinum foil electrode. The saturated calomel reference electrode and the platinum indicator electrode were connected to an R.C.A. ultrasensitive d.c. microammeter. The potential of the saturated calomel electrode was sufficiently

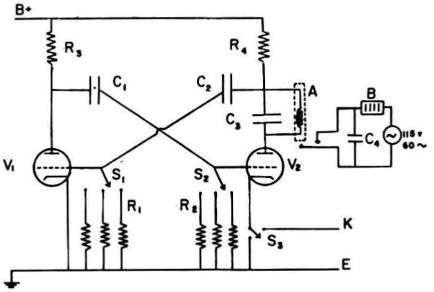


Fig. 1. Multivibrator circuit.

C_1	1 μF (mica);	*B*	Pic Electric Counter Model 6115A;
C_2	0.5 μF (mica);	*K* and *E*	connections to titration cell;
C_3	2 μF;	R_1	100 KΩ, 0.5 MΩ and 1.0 MΩ;
C_4	0.1 μF;	R_2	100 KΩ, 0.5 MΩ and 1.0 MΩ;
V_1 and V_2	6 SN7;	R_3	15 KΩ Ohmite 50 W;
A	Potter and Brumfield Plate Circuit Relay KCP 5/5 KΩ;	R_4	10 KΩ Ohmite 50 W.

TABLE I

VARIATION OF PULSE HEIGHT WITH R_1 AND R_2

$B+ = 250$ V; load $= 47\ \Omega$.

$R_1 : R_2$ (KΩ : KΩ)	*Maximum height (scale divisions)*	*Maximum height (scale divisions)*
100 : 100[a]	+ 9.1	—2.7
500 : 100	+ 8.0	—5.0
1000 : 100	+ 8.4	—4.4
100 : 500[a]	+11.2	—3.0
500 : 500	+ 7.5	—5.0
1000 : 500	+ 7.9	—4.5
100 : 1000	+11.4	—3.0
500 : 1000	+ 7.2	—5.0
1000 : 1000	+ 7.9	—4.2

[a] The rate of generation of pulses is not constant.

negative to give limiting currents which were proportional to the concentration of free bromine in solution. It was found convenient in some experiments to record the limiting current, and a Speedomax Type G recorder was used for this purpose. In all experiments the solution in the central titration vessel was stirred vigorously by means of a magnetic stirrer.

Electrodeposition of copper and silver

The pulse circuit and counting circuit were the same as that described by DEVANATHAN AND FERNANDO[1]. The power supply consisted of a conventional power pack with a full wave rectifier, choke and condensers regulated at 300 V with the aid of two VR 150 tubes. The current was supplied to all apparatus through a constant voltage transformer delivering 230 V a.c. at 50 cycles.

The cell in which electrodepositions were carried out consisted of a platinum crucible containing the electrolyte. The crucible was placed on a conducting surface and connected to the cathode. The anode consisted of a cylindrical block of silver 25 mm long and 12 mm in diameter to which was screwed a long silver rod 3 mm in diameter. This rod was clamped with the aid of a polythene sleeve insulator, so that the cylindrical anode was symmetrically placed in the electrolyte. A similar copper anode was used for the electrodeposition of copper.

In order to carry out electrodepositions at elevated temperatures, the platinum crucible was inserted into a cavity machined out of a brass hexagonal block, 10 cm high. This block was heated electrically on a hot-plate, the block being insulated from the hot-plate by a mica sheet. A thermometer pocket, in close proximity to the cavity in the brass block, registered the temperature of the bath solution.

Two different electrolytes were used in the electrodeposition of silver. The first electrolyte consisted of 250 ml of 0.1 M $AgNO_3$ to which concentrated ammonia was added until a faint permanent precipitate was obtained. To this solution, 30 g CH_3COONH_4 and 10 g NH_4NO_3 were added, and the resulting solution stirred thoroughly and filtered before use. The second electrolyte was prepared by mixing 250 ml of 0.1 M $AgNO_3$ and 250 ml of 0.5 M KCN. The solution was filtered before use. The electrodeposition of copper was carried out from the following solution: concentrated ammonia was added to 250 ml of 0.5 M $CuSO_4$, until a faint permanent precipitate was obtained. To this solution, 30 g CH_3COONH_4 and 10 g NH_4NO_3 were added and the resulting solution thoroughly stirred and filtered before use.

TABLE II

ELECTRODEPOSITION OF COPPER AND SILVER WITH CURRENT PULSES

Metal	*Time (min)*	*No. of pulses*	*Wt. of metal (mg)*	*No. of determinations*
Silver	30	2145 ± 8	17.91 ± 0.22	11
Silver	30	2146 ± 7	18.19 ± 0.21	14
Copper	60	4294 ± 11	10.24 ± 0.11	15
Copper	60	4290 ± 13	10.61 ± 0.03	6
With new tubes in multivibrator				
Silver	30	2327 ± 8	16.23 ± 0.15	15
Copper	60	4667 ± 8	8.75 ± 0.16	12

The pulse coulometer was switched on and allowed to warm up for about an hour with the cell connections short circuited. The high voltage supply to the multivibrator circuit was switched off leaving the filament current on. The connections to the coulometer were made and the high voltage supply switched on. Current pulses were passed for a fixed period of time, the high tension supply switched off, and the number of pulses passed was noted. The platinum crucible was washed repeatedly with distilled water until it was free of electrolyte, rinsed with methanol, dried at 130° in an oven, cooled in a desiccator and weighed on a microbalance to the nearest hundredth of a milligram. The results obtained are shown in Table II.

RESULTS

The shape and size of current pulses

The shape and size of current pulses obtained from the simple multivibrator circuit shown in Fig. 1 were studied on a cathode ray oscilloscope. The voltage across a resistance of 47 Ω connected between the points K and E, was applied to the Y plates of an oscilloscope with $R_1 : R_2 =$ 100 KΩ : 100 KΩ. Pulses were generated at a sufficiently rapid rate to permit the sweep frequency to be adjusted to give a stationary image on the screen, the general shape of which is shown in Fig. 2. Each pulse had a leading edge L over the flat portion of the pulse and a trailing edge T below the zero voltage line. The pulses were found to be of constant magnitude. The shape of the pulse was not altered significantly by disconnecting the relay and connecting the anode of V_2 to $B+$ through a bias of 10 KΩ. The maximum heights of the leading edge at a $B+$ of 250 V for each combination of R_1 and R_2 are given in Table I. An asterisk denotes those combinations which do not permit a steady generation of pulses at $B+ =$ 250 V.

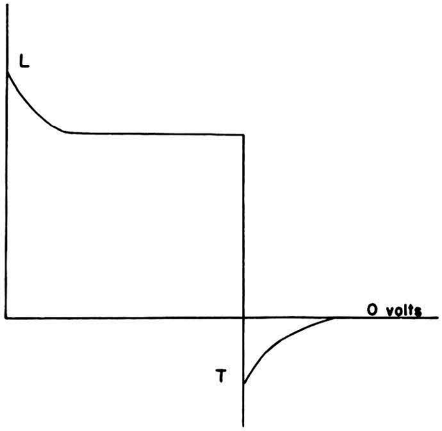


Fig. 2. Pulse shape obtained with multivibrator.

The above experiments showed that the shape of the pulses generated by this multivibrator was not ideal. If however the pulse size is constant for a given combination of R_1, R_2, C_1 and C_2, then the multivibrator could be used to electrogenerate a constant quantity of bromine with every pulse. The most direct method for testing the constancy of the pulse size obtained with this type of multivibrator is to electrodeposit silver or copper in a coulometer as described in the experimental section.

Twenty-five sets of data were obtained for the electrodeposition of silver and about twenty for copper. In the former case the time allowed for the electrodeposition was exactly 30 min, and the number of pulses registered for this period and the weight of the silver deposited were measured. Because copper has a small electrochemical equivalent, the time for the electrodeposition was increased to 60 min in order to get an appreciable deposit of copper. The results were analyzed statistically and the standard deviations are shown in Table II. The pulse size, calculated from the amount of silver deposited varies between $7.47 \cdot 10^{-3}$ and $7.57 \cdot 10^{-3}$ coulombs/pulse; when calculated from the amount of copper deposited, the pulse size is found to vary between $5.75 \cdot 10^{-3}$ and $5.96 \cdot 10^{-3}$ coulombs/pulse. The low result obtained for the pulse size from the electrodeposition of copper can be readily explained. The electrodeposited copper redissolves in the electrolyte during the time interval in which no current is passing through the coulometer, *i.e.*, during the time interval between two pulses. This reduces the total weight of copper electrodeposited and thereby gives rise to a smaller pulse size. The tendency for silver to redissolve in the electrolyte in this manner is small.

Table II shows the effect of using new tubes in the multivibrator circuit. On replacing the aged tubes with new ones, there was a considerable change in the pulse size.

In all electrodeposition experiments carried out under a variety of conditions, it was noticed that the deposits of silver and copper were crystalline and it would seem that the use of current pulses to electrodeposit metals, favors the formation of crystalline deposits.

The indicator electrode system

The pulse and counting circuits shown in Fig. 1 were used for the electrogeneration of bromine. Two indicator electrode systems were examined in this work, a platinum macroelectrode of area 5.38 cm^2 and a rotating platinum microelectrode. The optimum polarizing voltage that should be used with platinum electrode systems in solutions containing bromine and bromide ions, was first established. Polarizing voltages between +0.62 V and +0.22 V *vs.* the reference saturated calomel electrode, fall on the limiting current plateau of the current-voltage curve, obtained for the electroreduction of bromine to bromide ions at the platinum electrode. All polarizing voltages used in our experiments were within this optimum range.

In order to evaluate the response of the platinum macroelectrode to $Br^- - Br_2$ in solution, bromine was electrogenerated in solutions each containing 25 ml 0.5 *M* KBr and 25 ml 0.1 *M* HCl. After the generation of a definite amount of bromine, the current in this indicator circuit decreased continuously with time. If each current reading was taken at a definite time, say 15 sec after the electrogeneration of bromine was interrupted, plots of current against number of pulses could be obtained. Except for a slight initial curvature, these plots were linear. However their slopes were different for different modes of pretreatment of the platinum electrodes, and these slopes were not reproducible. Consequently variable titration blanks, from 0.3 to 6.0 pulses, were obtained.

When a platinum macroelectrode was employed as the indicator electrode, the current in the indicator circuit showed a decrease of 5.2 μA in 40 min, after a definite quantity of bromine was electrogenerated with 21 pulses. A similar experiment was carried out with a rotating platinum microelectrode; the same amount of bromine was electrogenerated (21 pulses) and the current in the indicator circuit showed a decrease of only 0.7 μA in 40 min. Furthermore, with a rotating platinum microelectrode, reproducible plots of the number of pulses *vs.* current in the indicator circuit, were obtained and the titration blanks were negligibly small. Hence, the rotating platinum microelectrode is much more satisfactory as an indicator electrode for the amperometric determination of bromine in spite of the fact that it has a lower sensitivity than the platinum electrode with a large surface area. In all bromometric titrations described in this work, the indicator electrode consisted of a rotating platinum microelectrode.

The condition of the surface of the platinum indicator electrode was an important factor which determined the precision and accuracy of coulometric titrations with electrogenerated bromine. The rotating platinum microelectrode in the indicator circuit as well as the platinum generator electrode in the bromine generating circuit were pretreated before every experiment by a method described by KOLTHOFF AND TANAKA[2]. An oxide film was first formed on the platinum surface when the electrode was immersed in concentrated nitric acid. The electrode was then washed thoroughly with distilled water and the oxide film reduced by placing the electrodes in a solution of ferrous sulfate. Finally, the electrodes were rinsed with distilled water and placed in the central compartment of the titration cell. The use of this pretreated electrode in the amperometric circuit for detecting the end-point in the bromometric titration of 8-quinolinol and arsenic(III), gave reproducible titration curves. Furthermore, titrations which were carried out in which the 8-quinolinol or As(III) were omitted, gave negligible blanks.

TABLE III

TITRATION OF 8-QUINOLINOL WITH ELECTROGENERATED BROMINE

$B+ = 250$ V; $R_1 : R_2 = 1$ MΩ : 1 MΩ

μg 8-quinolinol	*No. of pulses*	*No. of pulses per μg of 8-quinolinol*
500	455	0.910
400	367	0.918
300	272	0.907
250	232	0.928
200	183	0.915
150	139	0.927
100	99	0.990
50	49	0.980
40	39	0.975
20	21	1.050
$B+ = 200$ V; $R_1 : R_2 = 100$ KΩ : 100 KΩ		
500	3750	7.500
450	3406	7.569
350	2636	7.531
250	1886	7.544
200	1510	7.550
150	1137	7.580
50	400	8.000

Titration of 8-quinolinol

The central compartment of the titration cell contained 50 ml of solution which was made up as follows: 25 ml 0.5 *M* KBr, *x* ml of a standard solution of 8-quinolinol in 0.1 *M* HCl and (25—*x*) ml of 0.1 *M* HCl. In the multivibrator circuit $B+ = 250$ V and $R_1:R_2 = 1$ MΩ : 1 MΩ. A second set of results was obtained when $B+ = 200$ V and $R_1:R_2 = 100$ KΩ : 100 KΩ. An R.C.A. microammeter and a pretreated rotating platinum microelectrode were used in the indicator circuit. All current readings in the indicator circuit were taken 2 min after the interruption of the bromine generation since it was found that the current reached a steady value after this time interval had elapsed. The results obtained are given in Table III.

Titration of arsenic(III)

A solution containing As(III) was made up as follows: 15 ml 0.5 *M* KBr, 25 ml 1 *M* H_2SO_4 and the standard As(III) solution, made up to a volume of 50 ml. The multivibrator settings were $B+ = 200$ V and $R_1:R_2 = 100$ KΩ : 100 KΩ. The experimental technique employed was the same as that for the titration of 8-quinolinol, and the results obtained are shown in Table IV.

TABLE IV

TITRATION OF ARSENIC(III) WITH ELECTROGENERATED BROMINE

$B+ = 200$ V; $R_1:R_2 = 100$ KΩ : 100 KΩ

μg arsenic(III)	*No. of pulses*	*No. of pulses per μg arsenic(III)*
300	2177	7.257
180	1306	7.256
120	873	7.275
84	609	7.250
60	450	7.500
36	270	7.500
24	182	7.583

DISCUSSION

The attempts to determine the pulse size electrogravimetrically, using a copper coulometer, were unsuccessful since a certain amount of the electrodeposited copper redissolved in the electrolyte during a run. With a silver coulometer the pulse size, calculated from the results in Table II, is 8.507 ± 0.107 μg/pulse. Therefore, the percentage error is 1.26%, which is identical with the percentage error for the weight of the silver electrodeposited, when the time is kept constant. Since the percentage error in the pulse rate is 0.5%, it is reasonable to assume that the pulse size also is subject to the same percentage error. However, the observed percentage error for the pulse size is 2.5 times the expected error. This increased error may be due to a number of factors. The nature of the deposits formed was not ideal and considerable difficulties were involved in collecting, washing and drying these granular or crystalline deposits. It is also possible, just as in the case of copper, for the electrodeposited silver to redissolve in the electrolyte during the electrodeposition. A variation in the pulse size could also be caused by a variation in the voltage supplied by the power pack over a long period of time or a change in the tube characteristics in the multivibrator. The results in Table II show that the pulse size is dependent on the "age" of the tubes. If the "aged" tubes were replaced with new ones, the pulse size showed a considerable change.

It must be emphasized that most of the errors that have been mentioned are encountered on examining the long term stability of the instrument. The short term reproducibility of the pulse size is considerably better than 1%. For maximum accuracy and reproducibility, the pulse size should be calibrated with a standard solution of the substance to be titrated, before a series of determinations is carried out.

The pulse size obtained from the instrument, described in the first part of the experimental section and shown in Fig. 1, was determined by a number of methods. When $B+ = 250$ V and $R_1 : R_2 = 1\ \text{M}\Omega : 1\ \text{M}\Omega$ a silver coulometer gave a pulse size of $3.25 \cdot 10^{-3}$ coulombs/pulse. When a standard solution of 8-quinolinol was titrated using the same experimental conditions, the pulse size was found to be $2.92 \cdot 10^{-3}$ coulombs/pulse. When $B+ = 200$ V and $R_1 : R_2 = 100\ \text{K}\Omega : 100\ \text{K}\Omega$ the pulse size obtained by titrating a standard solution of 8-quinolinol was $3.54 \cdot 10^{-4}$ coulombs/pulse. If a standard solution of arsenic(III) was used, the pulse size was found to be $3.55 \cdot 10^{-4}$ coulombs/pulse. Therefore, in the titration of 8-quinolinol and arsenic(III) with electrogenerated bromine, the titration efficiency is 100%, under the experimental conditions used.

It is evident from this work that the direct determination of the pulse size using a silver coulometer is unreliable for reasons that have already been mentioned. Our results indicate that the electrogeneration of bromine is 100% efficient and the titration efficiency is 100% in the bromometric titration of 8-quinolinol and arsenic(III). However, Tables III and IV show that in order to titrate less than about 100 μg of 8-quinolinol, an excess of electrogenerated bromine is required. This effect has been reported previously[1] and confirmed repeatedly in this work. In the titration of arsenic(III) an increased quantity of bromine was required for the titration of quantities less than about 100 μg arsenic(III). The reason for this anomalous behavior is under investigation.

ACKNOWLEDGEMENT

This work was supported by a grant from the Research Corporation.

SUMMARY

A simplified multivibrator circuit has been constructed and the suitability of this simplified circuit for coulometric titrations has been investigated. The factors that affect the coulombic magnitude as well as the rate of generation of current pulses, have been evaluated. Arsenic(III) and 8-quinolinol have been titrated with electrogenerated bromine and a pretreated rotating platinum microelectrode has been shown to be the most suitable indicator electrode for detecting the end-point in these titrations.

REFERENCES

[1] M. A. V. Devanathan and Q. Fernando, *Trans. Faraday Soc.*, 52 (1956) 1332.
[2] I. M. Kolthoff and N. Tanaka, *Anal. Chem.*, 26 (1954) 632.

A SENSITIVE POLAROGRAPHIC TECHNIQUE

HARRY B. MARK, JR. AND CHARLES N. REILLEY

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

(Received February 13th, 1961)

INTRODUCTION

Conventional d.c. polarography using a dropping mercury electrode (DME) is usually limited to the analysis of solutions having concentrations of the reducible species which are greater than 10^{-5} *M*. Several modifications of the polarographic technique and apparatus, however, have been made which improve the sensitivity of analyses made with a DME[1,2]. A few of the more important methods are alternating current[3], square-wave[4], radio-frequency[4], and derivative[5] polarography. Also a few techniques have been developed which utilize the properties of the current transients in the DME during a portion of the lifetime of a single drop[1], these current transients being examined by means of an oscilloscope. Either a sawtooth[1,6] or a triangular[1,7] voltage scan can be applied to the DME during the last portion of the drop life, and the current-potential curve is observed. The foregoing methods, however, require special electronic equipment and the experimental procedures are often complicated.

The current transient during the life of a mercury drop at a fixed polarization potential is very easily obtained experimentally[8]. The current-time curve can be observed by measuring with an oscilloscope the voltage drop across the resistor in series with DME in the conventional d.c. polarograph circuit (at a fixed E). Strangely the curve obtained this way, however, has apparently never been used for the quantitative measurement of small concentrations. This paper describes two methods for making quantitative analyses from i-t polarograms for a single reducible component in solution at a concentration of 10^{-6} *M*. Also, a method for the qualitative and quantitative analysis of mixtures of reducible species in 10^{-6} *M* concentration is described.

THEORY

The theoretical equation for the instantaneous diffusion limited current, i_d, attributed to the reduction of a species at the surface of a dropping mercury electrode (DME), as derived by ILKOVIČ[9], is:

$$i_d = 706\, nD^{1/2}Cm^{2/3}t^{1/6}\ \mu\text{A} \tag{1}$$

where n is the number of electrons/atom transferred during the reduction, D is the diffusion coefficient of the reducible species in units of cm^2 sec^{-1}, C is the concentration of the reducible species in mmoles/l, m is the weight of mercury in mg flowing from the capillary per sec, and t is any instant of time during drop life and has the unit of sec. Although the ILKOVIČ equation has been found to be partially in error theoretically[10], and several other expressions for i_d have been derived[10,11,12], the theoretical i_d value calculated below from the ILKOVIČ equation is sufficiently accurate for the purposes of this paper.

Because i_d is directly proportional to C, it is very small (approximately $9.2 \cdot 10^{-3}\ \mu A$) for a solution containing $1.0 \cdot 10^{-6}\ M\ Pb^{2+}$ and $0.10\ M$ KCl [$n = 2$, $D = 0.98 \cdot 10^{-5}$ $cm^2\ sec^{-1}$[13], $m = 2.32$ mg sec^{-1}, and $t = 3.20$ sec].

The total current in a DME circuit at any instant during drop life is the sum of the diffusion limited current and a residual or background current, i_r. The residual current is, in turn, the sum of two currents:

$$i_r = i_c + i_f \qquad (2)$$

where i_c is the current which charges the double layer capacitance at the mercury-solution interface, and i_f is believed to be a small "faradaic" current caused by the reduction of very small amounts of impurities, such as oxygen or copper, from the distilled water in the solution[14]. The capacitance or charging current is given, as a function of time during the drop life, by[14]:

$$i_c = 0.0085\ K(E_{max} - E)m^{2/3}\,t^{-1/3}\ \mu A \qquad (3)$$

where K is the integral capacitance per unit area of the double layer, (μfd cm^{-2}), E_{max} is the electrocapillary maximum and E is the potential of the DME with respect to the reference electrode. In $0.10\ M$ KCl and for E more negative than E_{max}, K was found[15] to be 22.3 μfd cm^{-2}. Thus, for $E = -0.80$ V and $E_m = -0.52$ V *vs.* the S.C.E., $m = 2.32$ mg sec^{-1}, and $t = 3.20$ sec, i_c is calculated to be 0.063 μA. Thus, the ratio of i_d/i_c is 0.146 for a solution of $1.0 \cdot 10^{-6}\ M\ Pb^{2+}$ and $0.10\ M$ KCl, and the ratio of i_d/i_r will be even smaller. As shown in the next section, i_d/i_r was found experimentally to be approximately 0.071 for the above solution under the conditions specified above. Accurate determination of i_d in such a system, then, would be impossible with a conventional polarograph.

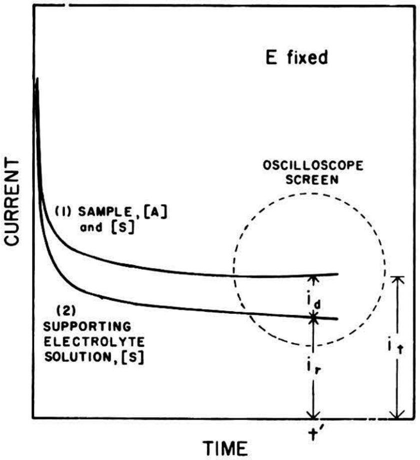


Fig. 1. The i–t curves obtained by the electrolysis at constant applied potential, E, of (1) a solution containing a concentration [A] of reducible species plus supporting electrolyte of concentration [S], and (2) supporting electrolyte only of concentration [S].

Because the total current, i_t, in the DME circuit when a solution of a reducible species, A, and a supporting electrolyte, S, is electrolyzed, is at any instant of time equal to $i_d + i_r$, a small i_d can be determined accurately only if both i_t and i_r can be measured accurately. I_r can be defined as the current, at the time t' during the drop life, when a solution of concentration (S) of supporting electrolyte is electrolyzed at a fixed potential E. I_t is then defined as the current at time t', when a solution of a concentration (A) of the reducible species plus supporting electrolyte of concentration (S) is electrolyzed at the same fixed potential, E. Hence, i_{d_A}, is equal to $i_t - i_r$ (see Fig. 1). E can be any potential at which the polarographic current due to A is diffusion limited.

The time, t', at which i_t and i_r are determined, should be very near the end of drop life, because the contribution of i_c to i_r is smallest at late values of t, and the i_d/i_r ratio is a maximum at the end of the drop life. Fig. 2 shows the relation (represented by the solid line) between the ratio i_d/i_r and time during the drop life for a typical solution. The error in i_d/i_r caused by an error in the time of measurement, $dt = \pm 25$ msec, is indicated by the two dashed lines. It is readily seen that the most reproducible values are also obtained at the end of the drop life. The primary reason for this is that the rate of change of current with time is at a minimum near the end of the drop life (see Fig. 1), and hence the current can be more reproducibly determined. Secondly, variations in current values attributed to stirring effects caused by the falling of the preceding mercury drop will decrease during drop life.

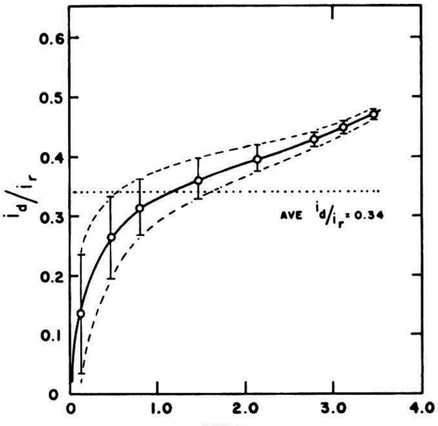


Fig. 2. The ratio of the diffusion current, i_d, to the residual current, i_r, as a function of time, t, during drop life: $[Pb^{2+}] = 6.60 \cdot 10^{-6}$ M; supporting electrolyte, 0.10 M KCl; $E = -0.80$ V *vs.* S.C.E.

The horizontal dotted line in Fig. 2 represents the average value of i_d/i_r (averaged over the drop life). This line also represents the value that would be obtained by means of an ordinary d.c. polarograph provided accurate and reproducible values of i_t and i_r at a fixed E could be obtained at such low current levels. Even so, the i_d/i_r ratio obtained in this way is not as large as the optimum value that can be determined at the end of the drop life by the methods proposed in this paper.

EXPERIMENTAL

Apparatus

The apparatus required is quite simple, as shown by the block diagram of Fig. 3. It is essentially a basic polarograph circuit, consisting of a dropping mercury electrode assembly (DME, saturated calomel reference electrode, and cell), a Rubicon model 2730 potentiometer, which serves as the variable polarization voltage source, and a series variable resistance box (R). The instantaneous current in the circuit is determined by measuring the voltage drop across R with an oscilloscope. Both a Du Mont type 350 oscillograph and a Tektronix type 502 oscilloscope were used, and each

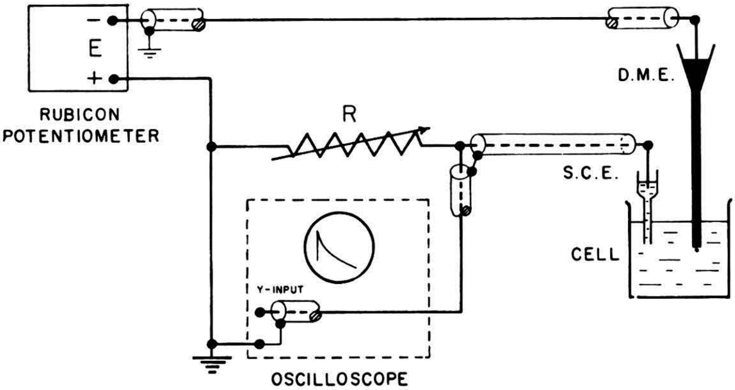


Fig. 3. Schematic diagram of sensitive polarograph circuit.

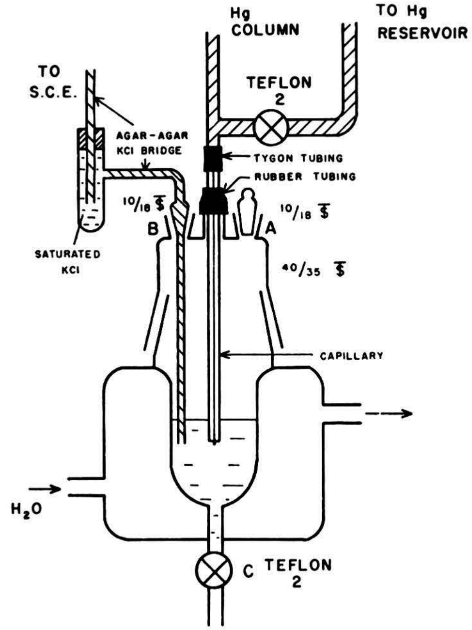


Fig. 4. Experimental arrangement of the polarograph cell.

proved to be satisfactory. The resistance R must be sufficiently large to produce voltage drops which can be detected by the particular oscilloscope used. All leads were shielded to eliminate 60-cycle pick-up by the circuit.

The details of the dropping-mercury electrode assembly are shown in Fig. 4. The drop time of the DME (in 0.1 M KCl with no applied potential) was 3.40 sec at a height of 48 cm of mercury. Under these conditions the mercury out flow m was 2.32 mg sec. The saturated calomel reference electrode made contact with the sample solution in the polograph cell through an agar–agar salt bridge, which was inserted into the cell through inlet B.

Procedure

The sample solution, 15 ml in volume, was introduced into the electrolysis cell through inlet A. The nitrogen delivery tube was then inserted through A, and nitrogen was bubbled through the solution for 10 min. to remove dissolved oxygen. The nitrogen delivery tube was then removed, and a stopper inserted in A to prevent oxygen from diffusing back into the electrolysis cell during the determination. During introduction of the sample and deaeration, the height of the mercury column above the capillary was reduced to prevent mercury drops from forming at the capillary tip eliminating oxidation of the mercury by the dissolved oxygen[3]. After the removal of oxygen, the mercury flow from the capillary tip was started by raising the mercury column to the desired height, and E was applied to the DME by means of the Rubicon potentiometer.

The oscilloscope was adjusted so that the portion of the i–t curve during the final 1/4 of drop life was displayed on the screen graticule (see Fig. 1), and the oscilloscope sweep was triggered by every other drop fall. The trace showed, then, the least sloping portion of the i–t curve, as well as the point at which the drop fell. In this way any fluctuations in drop time showed up as changes in the end-point of the i–t curve. The point, t', at which i_r and i_t were measured was arbitrarily chosen to be 0.20 sec before drop fall ($t' = 3.20$ sec). The i_r and i_t values were reproducible, if the error in t' was less than ± 20 msec.

As mentioned before, two types of oscilloscopes were used for the actual measurement of i_d. With the Du Mont type 350 oscillograph operated with a single ended input, the i–t curve obtained when a 0.10 M KCl supporting electrolyte solution was electrolyzed at a potential E was displayed on the screen graticule as described above, and i_r was determined at t'. The i–t curve resulting from the electrolysis of a solution of 10^{-6} M of a reducible species and 0.10 M KCl, was displayed on the graticule, and i_t determined at t' and E. The i_d for the concentration of the reducible species was then calculated as ($i_t - i_r$). Reproducible values of i_t, i_r and i_d were obtained provided the concentration of supporting electrolyte was the same in all solutions. It was found that drift of the oscilloscope trace, caused mainly by fluctuation in the a.c. line voltage, would introduce error in the i_d values obtained. A Thordarson type T-23701 automatic voltage regulator transformer placed in the a.c. line reduced the amount of drift but did not eliminate it. It was necessary, therefore, to measure i_r both before and after each measurement of i_t. If i_r remained constant, it was assumed that no drift occurred during the analysis. In this way, reproducible i_d values were obtained.

The usefulness of the above technique is limited in two ways. The number of operations needed to obtain reliable i_d values is quite large, and also i_r values become so large at E values more negative than -1.20 V that the i–t curves cannot be positioned on the screen (the y-axis position control can no longer oppose all the residual current). These limitations can be overcome by using, either the Du Mont 350 or the the Tektronix type 502 oscilloscope set for a differential or balanced input, giving a common mode rejection. The signal voltage developed across R is applied to the one side of the differential input of the oscilloscope and a voltage from a second Rubicon model 2730 potentiometer is applied to the other side of the input. In this way the instantaneous signal voltage corresponding to i_r can be balanced and i_r will correspond to the d.c. zero point on the screen graticule. The i_d values can, therefore, be measured directly, because they are equal to the difference between i_t and the d.c. zero point. A series of i_d determinations can be made more quickly by this technique, because only a check on the position of d.c. zero is needed to show if any drift has occurred.

The Tektronix oscilloscope has an added advantage in this case, because the measurement time, t', can be made with reference to the beginning of drop life instead of with the end of drop life. The calibrated sweep time of the Tektronix oscilloscope allows accurate time measurement at any point on the i–t curve when the sweep is triggered by the instantaneous positive voltage rise across R resulting from the formation of a new drop (see Fig. 1). Thus, it is not necessary to accurately adjust the drop time. It needs only to be greater than t'.

Calibration curves

Calibration of the instrument for three metal ions was made by plotting i_d values *versus* concentration. The Du Mont type 350 oscillograph was used to determine the i_d values for known concentrations of metal ion. It was found that the i_d–C plots were linear over a range of $1 \cdot 10^{-6}$ M to $10 \cdot 10^{-6}$ M for Cu^{2+} at $E = -0.35$ V *versus* the S.C.E., Pb^{2+} at $E = -0.80$ V and Zn^{2+} at $E = -1.20$ V. The i_d–C plot shown in Fig. 5 for Pb^{2+} is a typical example. None of the i_d *vs.* C plots were found to pass precisely through the origin on extrapolation to zero concentration. No explanation for this has yet been proposed.

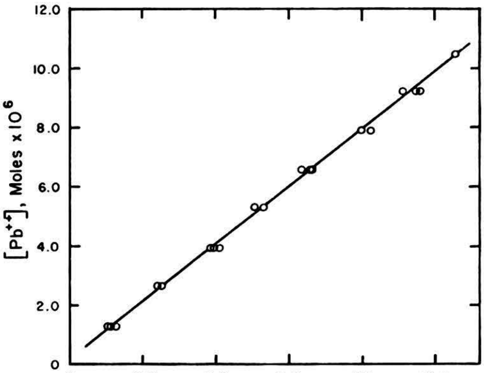


Fig. 5. Typical calibration curve for Pb^{2+} in 0.10 M KCl: drop time = 3.40 sec; supporting electrolyte, 0.10 M KCl; $E = -0.80$ V *vs.* S.C.E.

Preparation of standard metal ion samples

The series of Cu^{2+}, Pb^{2+} and Zn^{2+} standard solutions ($1.0 \cdot 10^{-6}$ *M* to $10 \cdot 10^{-6}$ *M*) were prepared by volumetric dilution of 10^{-4} *M* stock solutions of these ions with distilled water and 1.0 *M* KCl (the standard solutions had a final concentration of 0.10 *M* KCl). The stock Cu^{2+} solution was prepared by dissolving a weighed sample of reagent grade copper wire in dilute reagent grade HNO_3 and diluting to volume with distilled water. The stock Pb^{2+} solution was made by dissolving with distilled water a weighed sample of reagent $Pb(NO_3)_2$ which had been recrystallized three times from water. The stock Zn^{2+} solution was prepared by dissolving a weighed sample of analytical reagent zinc metal with dilute HNO_3 and diluting to volume with distilled water.

A stock solution of 1.0 *M* KCl was made from reagent grade KCl and distilled water. Aliquots from this stock KCl solution were used to prepare all the standard solutions of metal ions.

APPLICATIONS

Analysis of solutions containing one reducible species

Once a diffusion current-concentration calibration plot (see Fig. 5) has been determined for a reducible species, solutions containing that species can be readily analyzed by determining i_d and reading the concentrations from the calibration plot. Some typical analyses on three metal ions, Cu^{2+}, Pb^{2+} and Zn^{2+}, are shown in Table I. The maximum error was $\pm 0.4 \cdot 10^{-6}$ *M*.

TABLE I

ANALYSIS OF SOLUTIONS CONTAINING A SINGLE REDUCIBLE METAL ION IN 10^{-6} *M* CONCENTRATIONS

Supporting electrolyte was 0.10 *M* KCl

Ion	*Polarization potential, E (V)*	*True concentration ($M \cdot 10^6$)*	*Measured concentration ($M \cdot 10^6$)*	*Deviation ($M \cdot 10^6$)*
Pb^{2+} $(NO_3)_2^-$	—0.80	6.60	6.5	—0.1
		2.64	2.5	—0.1
		1.32	1.6	+0.3
		3.96	4.2	+0.2
		9.24	9.5	+0.3
Cu^{2+} $(NO_3)_2^-$	—0.35	0.99	1.2	+0.2
		4.94	4.9	0.0
		1.98	2.3	+0.3
		3.94	3.7	—0.2
		9.87	9.8	—0.1
Zn^{2+} $(NO_3)_2^-$	—1.20	9.75	10.1	+0.4
		7.32	7.3	0.0
		2.45	2.2	—0.3

Qualitative analysis of solutions containing several reducible species

It was found that solutions containing a mixture of two or more reducible species in 10^{-6} *M* concentrations can be quickly analyzed qualitatively using the Tektronix Type 502 oscilloscope, provided that the half-wave potentials of the species are sufficiently different ($\Delta E_{1/2} = 0.2$ V or greater). The drop time of the DME is adjusted so that it is greater than t' at any value of E in the potential range used. A current–potential curve is first determined for the supporting electrolyte solution alone. With E initially at a potential 0.2 V more positive than the most positive $E_{1/2}$ for any of the species in the mixture (at this E, i_r is equal to the current of the mixture), E is made increasingly negative in 0.05 V steps. The residual current, i_r, caused by the supporting electrolyte is determined at each E value, and i_r *vs.* E is plotted. Such a plot for 0.10 M KCl is shown by curve 1 of Fig. 6. The i_t–E curve for the electrolysis of the mixture (including the supporting electrolyte) is obtained in the same manner. Curve 2 of Fig. 6 is an i_t–E curve obtained by the electrolysis of a solution of $6.60 \cdot 10^{-6}$ M Pb^{2+}, $7.31 \cdot 10^{-6}$ M Zn^{2+} and 0.10 M KCl. The graphical difference between the i_t–E and the i_r–E curves is the polarogram of the reducible species in the mixture. The number of waves indicates the number of different species, and approximate $E_{1/2}$ values for each species can be determined from each wave. Curve 3 of Fig. 6 shows two sharp waves (for Pb^{2+} and Zn^{2+}) and the $E_{1/2}$ values obtained from the waves are approximately —0.42 V and —1.05 V *versus* the S.C.E. These values are reasonably close to the reported values of —0.40 V *versus* the S.C.E. for Pb^{2+} in 0.1 M KCl[16] and —0.995 V *versus* the S.C.E. for Zn^{2+} in 0.1 M KCl[17]. The experimental $E_{1/2}$ values can, therefore, be used to identify the species in a solution.

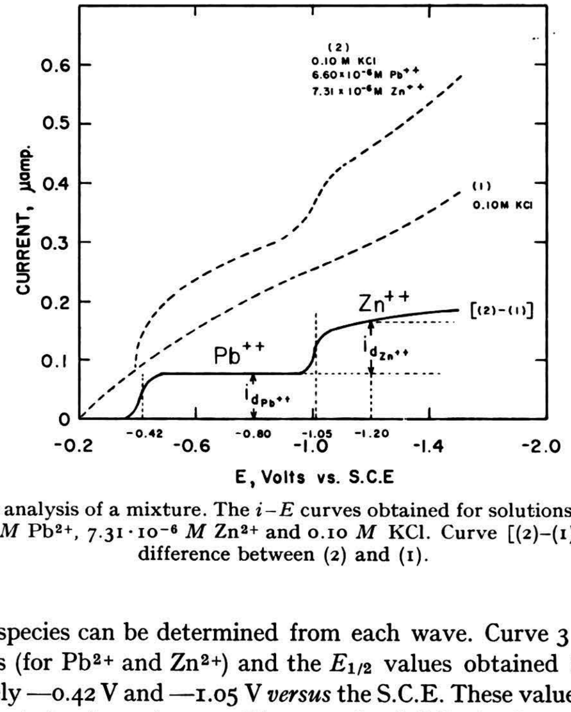


Fig. 6. Qualitative analysis of a mixture. The i–E curves obtained for solutions of (1) 0.10 M KCl and (2) $6.60 \cdot 10^{-6}$ M Pb^{2+}, $7.31 \cdot 10^{-6}$ M Zn^{2+} and 0.10 M KCl. Curve [(2)–(1)] is the graphical difference between (2) and (1).

The concentration of each reducible species in a mixture can be estimated, provided that the identity of each species is known and calibration plots for each species have been constructed. The wave height, i_d, of each wave is measured at the E values used in constructing the i_d–C plots (see Fig. 6), and C is read from i_d–C plots. The concentration values obtained in this manner are not quantitative because drift of the oscilloscope trace during the determination cannot be easily detected and this contributes to the overall error.

Quantitative analysis of mixtures

A solution containing two or more reducible species (A, B, . . .) can be analyzed quantitatively, provided that the identity of each species is known, and that the $E_{1/2}$ values for the various species differ by at least 0.2 V. The diffusion current for the species having the most positive $E_{1/2}$ (assume this to be species A) can be determined by the technique described above for the analysis of a single reducible component solution, because none of the other species in the mixture are reduced at the polarization potential, E_A, which reduces A. The value of t' and E_A, however, must be the same as those used to construct a calibration plot for A.

A solution containing the same concentrations of A and of the supporting electrolyte as the mixture is then prepared and the current i_r', is determined for the same potential and t' as was used to construct an i_d–C plot for species B. The current, i_t, obtained when the mixture is electrolyzed at E_B is then determined. The diffusion current, i_{d_B}, caused by the species B is, therefore, equal to $i_t - i_r'$ at E_B because

$$(i_r') \text{ at } E_B = (i_{d_A} + i_r) \text{ at } E_B \tag{4}$$

and

$$(i_t) \text{ at } E_B = (i_{d_B} + i_{d_A} + i_r) \text{ at } E_B \tag{5}$$

Thus,

$$(i_t - i_r') \text{ at } E_B = (i_{d_B}) \text{ at } E_B \tag{6}$$

$[B]$ is then read from the i_{d_B}–C_B plot.

A solution containing $[A]$, $[B]$, and the supporting electrolyte is then prepared, electrolyzed at E_c, and, thus, (i_r') at E_c is determined. Next, (i_t) at E_c is measured, and i_{d_c} is then equal to

$$(i_{d_c}) \text{ at } E_c = (i_t - i_r') \text{ at } E_c \tag{7}$$

by the same argument presented above. If other components are present in the mixture, their concentrations are determined by continuation of this procedure.

Table II shows the results of a few typical analyses, by this method, of solutions containing Cu^{2+}, Pb^{2+} and Zn^{2+} in 10^{-6} M concentration, using 0.10 M KCl as the supporting electrolyte. Although any error introduced in the determination of $[A]$

TABLE II

ANALYSIS OF SOLUTION CONTAINING Cu^{2+}, Pb^{2+} AND Zn^{2+} IN 10^{-6} M CONCENTRATIONS

0.10 M KCl supporting electrolyte

Mixture No.	*Ion*	*Polarisation potential, E (V)*	*True concentration ($M\cdot 10^6$)*	*Measured concentration ($M\cdot 10^6$)*	*Deviation ($M\cdot 10^6$)*
1	Cu^{2+}	—0.35	4.94	5.3	+0.4
	Pb^{2+}	—0.80	6.60	6.8	+0.2
	Zn^{2+}	—1.20	4.88	5.4	+0.5
2	Cu^{2+}	—0.35	2.94	5.0	+0.1
	Pb^{2+}	—0.80	2.64	2.4	—0.2
	Zn^{2+}	—1.20	7.31	7.7	+0.4
3	Cu^{2+}	—0.35	2.96	2.9	—0.1
	Pb^{2+}	—0.80	6.60	5.8	—0.8
	Zn^{2+}	—1.20	2.44	2.8	+0.4

(in this case [Cu^{2+}]) affects the values obtained in the subsequent determinations, the maximum error found in concentration values of the subsequent species was $\pm 0.8 \cdot 10^{-6}$ *M*.

DISCUSSION

The method described above is a simple and relatively inexpensive way of measuring with the DME the concentration of a reducible species in solution in the 10^{-6} *M* range. The method described for analyzing a solution containing a single reducible species is capable of detecting concentration changes of 3 to $4 \cdot 10^{-7}$ *M*. This sensitivity is as good or better than that obtained by saw-tooth wave $1 \cdot 10^{-5}$ *M*[18], triangular voltage scan (about $1 \cdot 10^{-6}$ *M*)[7], derivative ($1 \cdot 10^{-6}$ *M*)[5] and differential (0.5 to $1.0 \cdot 10^{-6}$ *M*)[19] polarography. Although the present method is not as sensitive as square-wave ($0.4 \cdot 10^{-7}$ *M*)[4], radio-frequency ($0.1 \cdot 10^{-7}$ *M*)[4], and alternating current (about $0.1 \cdot 10^{-7}$)[20] polarography, the relative simplicity of the experimental procedure and apparatus used to obtain i–t curves is a considerable advantage in applications where the ultimate in sensitivity is not required.

ACKNOWLEDGEMENT

This research was sponsored in part by the U.S. Air Force, Office of Scientific Research and Development Command, under Contract No. AF 49(638)-333.

SUMMARY

A simple polarographic technique, based upon measuring the difference between the total current in the sample solution and the residual current in the supporting electrolyte solution at a specified time during drop life, was investigated. Concentrations, ranging from 10^{-6} to 10^{-5} *M*, of a single reducible species could be determined to within $\pm 0.4 \cdot 10^{-6}$ *M*. A similar technique permits qualitative and quantitative analysis of mixtures containing two or more reducible species in the 10^{-6} *M* concentration range. These methods were tested with solutions of Pb^{2+}, Cu^{2+} and Zn^{2+}.

REFERENCES

[1] J. W. LOVELAND AND P. J. ELVING, *Chem. Revs.*, 51 (1952) 67.
[2] D. N. HUME, *Anal. Chem.*, 32 (1960) 137R.
[3] H. H. BAUER AND P. J. ELVING, *Anal .Chem.*, 30 (1958) 334.
[4] G. C. BARKER, *Anal. Chim. Acta*, 18 (1958) 118.
[5] M. T. KELLY AND D. J. FISHER, *Anal. Chem.*, 30 (1958) 929.
[6] J. E. B. RANDLES, *Trans. Faraday Soc.*, 44 (1948) 327.
[7] A. SEVCIK, *Collect. Czechoslov. Chem. Communs.*, 13 (1948) 349.
[8] H. A. MCKENZIE, *Australian J. Chem.*, 11 (1958) 271.
[9] D. ILKOVIČ, *Collect. Czechoslov. Chem. Communs.*, 6 (1934) 498.
[10] J. J. LINGANE AND B. A. LOVERIDGE, *J. Am. Chem. Soc.*, 72 (1950) 438.
[11] J. KOUTECKY, *Csl. Cas. Fys.*, 2 (1952) 117.
[12] M. VON STACKELBERG, *Z. Elektrochem.*, 57 (1953) 338.
[13] I. M. KOLTHOFF AND J. J. LINGANE, *Polarography*, Vol. I, 2nd edn., Interscience Publishers, Inc., New York, 1947, p. 95.
[14] I. M. KOLTHOFF AND J. J. LINGANE, *Polarography*, Vol. I, 2nd edn., Interscience Publishers, Inc., New York, 1947, p. 147.
[15] D. ILKOVIČ, *Collect. Czechoslov. Chem. Communs.*, 8 (1936) 170.
[16] L. MEITES, *Polarographic Techniques*, Interscience Publishers, Inc., New York, 1955, p. 269.
[17] I. M. KOLTHOFF AND J. J. LINGANE, *Polarography*, Vol. II, 2nd edn., Interscience Publishers, Inc., New York, 1952, p. 504.
[18] F. C. SNOWDEN AND H. T. PAGE, *Anal. Chem.*, 22 (1950) 969.
[19] J. HEYROVSKY, *Anal. Chim. Acta*, 2 (1948) 533.
[20] F. V. STURM, *Z. anal. Chem.*, 166 (1959) 100.

CHRONOPOTENTIOMETRY WITH CURRENT PROGRAMMED AS A FUNCTION OF TIME

I. CONSTANT POWER FUNCTIONS OF TIME

ROYCE W. MURRAY AND CHARLES N. REILLEY

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

(Received March 14th, 1961)

INTRODUCTION

Chronopotentiometric techniques, in general, may be said to consist of the application of a programmed current function to an electrode with subsequent measurement of its potential as a function of time. This definition places no restriction on the nature of the current function employed. Because of the growing importance of chronopotentiometry in kinetic studies at electrodes and in solution, efforts have been made to extend the applicability of chronopotentiometry through the use of current functions other than the simple application of constant current. These have included linear current scan and changes in the current function at some time during the experiment (such as current reversal). For semi-infinite linear diffusion processes,theoretical equations have been reported for the following current functions:

(A) constant current with current reversal[1];
(B) constant current with changes in current at any time[2];
(C) current varying with the square root of time[3-7];
(D) current varying linearly with time[8-9].

In the case of constant current with current reversal, theoretical equations have also been derived for situations where kinetic complications exist[10-12]. Several studies of chemical systems have been made using this technique[11-14]. Chronopotentiometric equations for linear finite diffusion have been derived and have been applied to electrodes designed for this diffusion case[9].

The growth of chronopotentiometric theory, as evidenced by the above examples, has been restricted rather severely as to the type and number of current functions used. Obviously it would be of considerable advantage to have available chronopotentiometric equations which are generalized as to the type and number of current functions used. Some current functions which would be of interest to consider in this respect would include any simple mathematical function of time such as exponential, trigonometric, logarithmic, repetitive (square wave, sawtooth), and power functions. Furthermore, one should consider step changes in the type and number of current functions employed. Another intriguing aspect lies in the consideration of the determination of the type or combination of current functions necessary to achieve any specified relationship between transition time and sample composition.

This paper presents an inquiry into the chronopotentiometric equations obtained for a single current function which is a power function of time. This represents the first paper in a series which will consider the application of a variety of single and combined current functions. The integral equation of KAMBARA AND TACHI[4] represents an attempt to establish this general viewpoint, but an explicit solution was not given by these authors for the general case. The type of mass transfer process to be considered in this paper is restricted to semi-infinite linear diffusion.

THE CASE OF A SINGLE SPECIES

For simplicity, the general equation for a single electroactive species will be treated first. The reaction to be considered will be denoted by

$$A \xrightarrow{\pm ne} B \tag{1}$$

The current function employed is a power function of time and is denoted as

$$i = \beta t^r \tag{2}$$

where i is the impressed current density (A/cm^2), β is the current-time proportionality constant (A/cm^2 sec^r), and r is any number greater than —1. The initial and boundary conditions for the solution of FICK's second law:

$$\frac{\partial A\,(x,t)}{\partial t} = D_A \frac{\partial^2 A\,(x,t)}{\partial x^2} \tag{3}$$

will be

$$A\,(x,0) = A^\circ, \quad t = 0 \tag{4}$$

$$A\,(x,t) = A^\circ, \quad t > 0, \quad x \to \infty \tag{5}$$

$$\left(\frac{\partial A\,(x,t)}{\partial x}\right)_{x=0} = \frac{\beta t^r}{nFD_A}, \quad t > 0 \tag{6}$$

where the symbols have their normal significance. The LAPLACE Transform will be used to effect the solution for these boundary conditions. Noting that the general transform of the boundary condition 6 is

$$L\left\{\left(\frac{\partial A\,(x,t)}{\partial x}\right)_{x=0}\right\} = \left(\frac{\partial \bar{A}\,(x,P)}{\partial x}\right)_{x=0} = \frac{\beta\Gamma(r+1)}{nFD_A P^{r+1}} \tag{7}$$

one may arrive at an explicit solution for the concentration of the reactant in the transform plane, $\bar{A}\,(x,p)$

$$\bar{A}\,(x,p) = \frac{A^\circ}{P} - \frac{\beta\Gamma(r+1)}{nFD_A{}^{1/2}P^{r+3/2}}\,e^{-xp^{1/2}/D_A^{\frac{1}{2}}} \tag{8}$$

where Γ denotes the *gamma* function.

Integral and half-integral values of r

The inverse transform of eqn. 8 can be readily found in tables for integral and half-integral values of r. The solution for $A\,(x,t)$ is

$$A\,(x,t) = A^\circ - \frac{\beta\,(4t)^{r+1/2} i^{2r+1} \Gamma(r+1)}{nFD_A{}^{1/2}} \operatorname{erfc} \frac{x}{2D_A{}^{1/2}t^{1/2}} \tag{9}$$

This equation can be converted into a more convenient form by means of the relation

$$2(2r+1)i^{2r+1}\operatorname{erfc}\lambda = i^{2r-1}\operatorname{erfc}\lambda - 2\lambda i^{2r}\operatorname{erfc}\lambda \tag{10}$$

By use of eqn. 10 and setting $x = 0$ to obtain the concentration at the electrode surface, two equations are obtained depending upon whether r is integral or half-integral:

r = integral

$$A\,(0,t) = A^\circ - \frac{\beta(4t)^{r+1/2}\Gamma(r+1)}{2^r nFD_A{}^{1/2}\pi^{1/2}} \prod_{r=0,1,2,}^{r} \left(\frac{1}{2r+1}\right) \tag{11}$$

r = half-integral

$$A\,(0,t) = A^\circ - \frac{\beta(4t)^{r+1/2}\Gamma(r+1)}{2^{r+1/2} nFD_A{}^{1/2}} \prod_{r=1/2,3/2,}^{r} \left(\frac{1}{2r+1}\right) \tag{12}$$

By use of the following equations for the Γ functions:

$r = 0$

$$\Gamma(1) = 1 \tag{13}$$

r = integral

$$\Gamma(r+1) = \prod_{r=1,2,}^{r} (r) \tag{14}$$

r = half-integral

$$\Gamma(r+1) = \frac{\pi^{1/2}}{2^{r+1/2}} \prod_{r=1/2,3/2,}^{r} (2r) \tag{15}$$

this now results in the final equations:

$r = 0$

$$A\,(0,t) = A^\circ - \frac{2\beta t^{1/2}}{nFD_A{}^{1/2}\pi^{1/2}} \tag{16}$$

r = integral

$$A\,(0,t) = A^\circ - \frac{2^{r+1}\beta t^{r+1/2}}{nFD_A{}^{1/2}\pi^{1/2}} \prod_{r=1,2,}^{r} \left(\frac{r}{2r+1}\right) \tag{17}$$

r = half-integral

$$A\,(0,t) = A^\circ - \frac{\pi^{1/2}\beta t^{r+1/2}}{nFD_A{}^{1/2}} \prod_{r=1/2,3/2,}^{r} \left(\frac{2r}{2r+1}\right) \tag{18}$$

The relationships between concentration and transition time may be evaluated from these equations by setting $A\,(0,t) = 0$. This yields

$r = 0$

$$\tau^{1/2} = \frac{nFD_A{}^{1/2}\pi^{1/2}A^\circ}{2\beta} \tag{19}$$

r = integral

$$\tau^{r+1/2} = \frac{nFD_A^{1/2}\pi^{1/2}A^\circ}{2^{r+1}\beta} \prod_{r=1,2,}^{r} \left(\frac{2r+1}{r}\right) \tag{20}$$

r = half-integral

$$\tau^{r+1/2} = \frac{nFD_A^{1/2}A^\circ}{\pi^{1/2}\beta} \prod_{r=1/2,3/2,}^{r} \left(\frac{2r+1}{2r}\right) \tag{21}$$

General case, r is any number > -1

Under the assumption that x may be set equal to zero in eqn. 8 prior to obtaining the inverse LAPLACE Transform, one may obtain a more general solution for $A\,(0,t)$ in which r may be any number > -1.

$$A\,(0,t) = A^\circ - \frac{\beta t^{r+1/2}\Gamma(r+1)}{nFD_A^{1/2}\Gamma(r+3/2)} \tag{22}$$

In a similar way the concentration of the product, $B\,(0,t)$, may be obtained

$$B\,(0,t) = B^\circ + \frac{\beta t^{r+1/2}\Gamma(r+1)}{nFD_B^{1/2}\Gamma(r+3/2)} \tag{23}$$

From eqn. 22 the general equation for the relationship between concentration and transition time is

$$\tau^{r+1/2} = \frac{nFD_A^{1/2}A^\circ\Gamma(r+3/2)}{\beta\Gamma(r+1)} \tag{24}$$

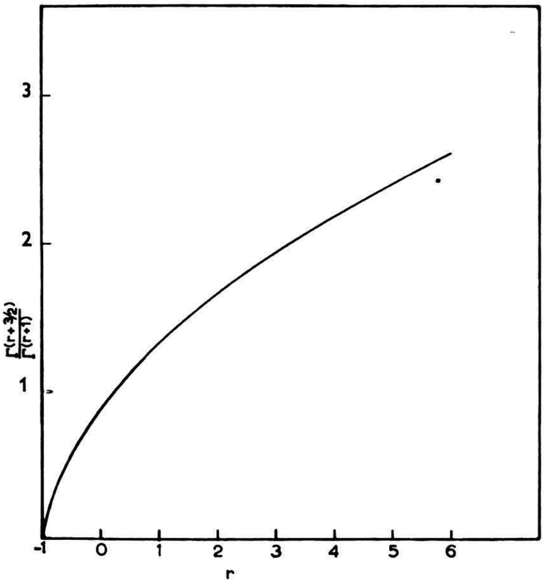


Fig. 1. Value of $\Gamma(r+3/2)/\Gamma(r+1)$ as a function of r.

The evaluation of eqn. 24 for integral and half-integral values of r yields equations identical to eqns. 19, 20 and 21. This lends validity to the assumption made in the derivation of eqn. 24. The ratio of the Γ functions in eqn. 24 can be readily evaluated from available tables. The variation of this ratio with r is given in Fig. 1. It is of interest to note that the power of the transition time is related very simply to the current function employed and to the concentration. For currents varying with the square root of time, ($r = 1/2$), the transition time, τ, varies linearly with the concentration, C. It is also interesting that when $r = -1/2$ one is operating under the conditions of chronoamperometry, as will be discussed below.

THE CASE OF MULTICOMPONENT MIXTURES

A system which contains several electroactive species will yield reactions which may be represented as

$$\begin{array}{c} A_1 \xrightarrow{\pm n_1 e} B_1 \\ \cdots\cdots\cdots \\ A_m \xrightarrow{\pm n_m e} B_m \end{array} \tag{25}$$

FICK's law corresponding to these reactions may be denoted as

$$\sum_{m=1,2,}^{m} \frac{\partial A_m(x,t)}{\partial t} = \sum_{m=1,2,}^{m} D_m \frac{\partial^2 A_m(x,t)}{\partial x^2} \tag{26}$$

The initial condition in this case is given by

$$\sum_{m=1,2,}^{m} A_m(x,0) = \sum_{m=1,2,}^{m} A_m^{\circ}, \quad t = 0 \tag{27}$$

and the boundary conditions by

$$\sum_{m=1,2,}^{m} A_m(x,t) = \sum_{m=1,2,}^{m} A_m^{\circ}, \quad t > 0,\ x \to \infty \tag{28}$$

$$\sum_{m=1,2,}^{m} n_m D_m \left(\frac{\partial A_m(x,t)}{\partial x}\right)_{x=0} = \frac{\beta t^r}{F}, \quad t > 0 \tag{29}$$

Solution of eqn. 26 under these initial and boundary conditions in a manner analogous to the above yields

$$\sum_{m=1,2,}^{m} n_m D_m^{1/2} A_m(0,t) = \sum_{m=1,2,}^{m} n_m D_m^{1/2} A_m^{\circ} - \frac{\beta t^{r+1/2} \Gamma(r+1)}{F\Gamma(r+3/2)} \tag{30}$$

Eqn. 30 is then employed to determine the transition times. The time required to obtain the transition time for the mth species is given by

$$\left\{\sum_{m=1,2,}^{m} \tau_m\right\}^{r+1/2} = \frac{F\Gamma(r+3/2)}{\beta\Gamma(r+1)} \sum_{m=1,2,}^{m} n_m D_m^{1/2} A_m^{\circ} \tag{31}$$

From eqn. 31 we can then write

$$\left\{\sum_{m=1,2,}^{m} \tau_m\right\}^{r+1/2} - \left\{\sum_{m=1,2,}^{m-1} \tau_m\right\}^{r+1/2} = \frac{n_m F D_m^{1/2} A_m^{\circ} \Gamma(r+3/2)}{\beta\Gamma(r+1)} \tag{32}$$

The quantity on the right corresponds to the transition time function that would have been obtained had the mth species been present alone. Thus from a chronopotentiogram of a multicomponent system one may evaluate the concentration of any given species provided that the transition times for the given species and the one preceding it are sufficiently well defined. In cases where a given species reacts in a multistep manner (*i.e.* more than two stable oxidation states), one may employ eqn. 32 by inserting the appropriate values of n.

By similar mathematical steps one obtains the concentration of products at the electrode surface, $B(0,t)$

$$\sum_{m=1,2,}^{m} n_m D_m^{\frac{1}{2}} B_m(0,t) = \sum_{m=1,2,}^{m} n_m D_m^{\frac{1}{2}} B_m^\circ + \frac{\beta t^{r+1/2}\Gamma(r+1)}{F\Gamma(r+3/2)} \tag{33}$$

POTENTIAL-TIME EQUATIONS

Reversible

If the electrode process is reversible, the potential of the working electrode is determined by the surface concentrations of the oxidized and reduced forms. Substitution of these concentrations, given by eqns. 22 and 23, into the NERNST equation yields

$$E = E_{1/2} + \frac{RT}{nF} \ln \frac{\tau^{r+1/2} - t^{r+1/2}}{t^{r+1/2}} \tag{34}$$

where $E_{1/2}$ is the polarographic half-wave potential given by

$$E_{1/2} = E^\circ + \frac{RT}{nF} \ln \frac{\gamma_A D_B^{1/2}}{\gamma_B D_A^{1/2}} \tag{35}$$

It may be deduced from eqn. 34 that the time at which the potential of the electrode is equal to $E_{1/2}$ is

$$t' = \left(\frac{1}{2}\right)^{\frac{2}{2r+1}} \tau \tag{36}$$

Some pertinent transition time and potential-time relationships are summarized in Table I for a few integral and half-integral values of r. The shape of the potential-time relation as a function of time is shown in Fig. 2 for selected cases of r. In Fig. 3 is shown the variation of the term t'/τ, ($E = E_{1/2}$), as a function of r. A more detailed discussion is given later.

Totally irreversible

For a totally irreversible electrode reaction, the relationship between current and potential is given by

$$i = nFk_f^\circ A(0,t)\, e^{\frac{-\alpha n_A F}{RT}E} \tag{37}$$

Substituting the value of the surface concentration of A (eqn. 22) and the current-time relationship (eqn. 2) into this expression yields

$$E = \frac{RT}{\alpha n_A F} \ln \frac{k_f^\circ \Gamma(r+1)}{D_A^{1/2}\Gamma(r+3/2)} + \frac{RT}{\alpha n_A F} \ln \frac{\tau^{r+1/2} - t^{r+1/2}}{t^r} \tag{38}$$

TABLE I

TRANSITION–TIME AND POTENTIAL–TIME RELATIONS

r	$\tau^{r+1/2}$	Q[a]	t'/τ[b]
0	$\frac{nFD^{1/2}\pi^{1/2}A^\circ}{2\beta}$	$\frac{\tau^{1/2}-t^{1/2}}{t^{1/2}}$	0.250
1/2	$\frac{2nFD^{1/2}A^\circ}{\pi^{1/2}\beta}$	$\frac{\tau-t}{t}$	0.500
1	$\frac{3nFD^{1/2}\pi^{1/2}A^\circ}{4\beta}$	$\frac{\tau^{3/2}-t^{3/2}}{t^{3/2}}$	0.630
3/2	$\frac{8nFD^{1/2}A^\circ}{3\pi^{1/2}\beta}$	$\frac{\tau^2-t^2}{t^2}$	0.706
2	$\frac{15nFD^{1/2}\pi^{1/2}A^\circ}{16\beta}$	$\frac{\tau^{5/2}-t^{5/2}}{t^{5/2}}$	0.759
5/2	$\frac{16nFD^{1/2}A^\circ}{5\pi^{1/2}\beta}$	$\frac{\tau^3-t^3}{t^3}$	0.793

[a] $E = E_{1/2} + RT/nF \ln Q$.
[b] t' is the time at $E = E_{1/2}$.

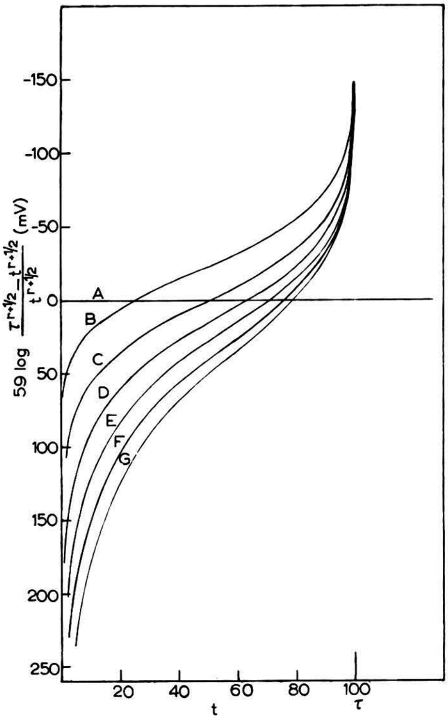


Fig. 2. Chronopotentiograms for a reversible electrode reaction: $\tau = 100$ sec; $T = 25°$; $n = 1$; (A) $r = -1/2$; (B) $r = 0$; (C) $r = 1/2$; (D) $r = 1$; (E) $r = 3/2$; (F) $r = 2$; (G) $r = 5/2$.

At large values of r, the time dependent log term in eqn. 38 approaches that of the reversible case (eqn. 34). Hence at large values of r, the chronopotentiograms for reversible and irreversible systems will be similar in shape, provided that the differ-

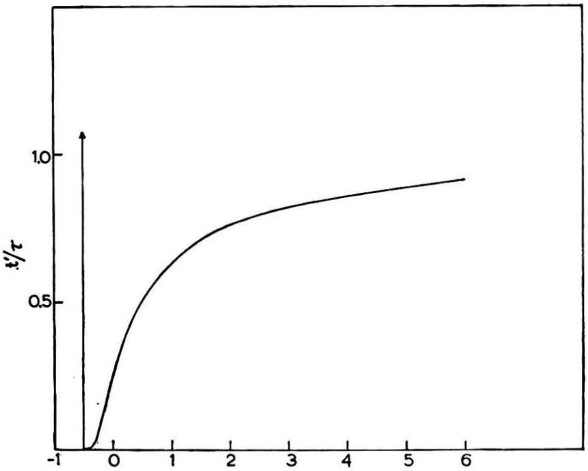


Fig. 3. Ratio of time, $t'(E = E_{1/2})$, and τ as a function of r.

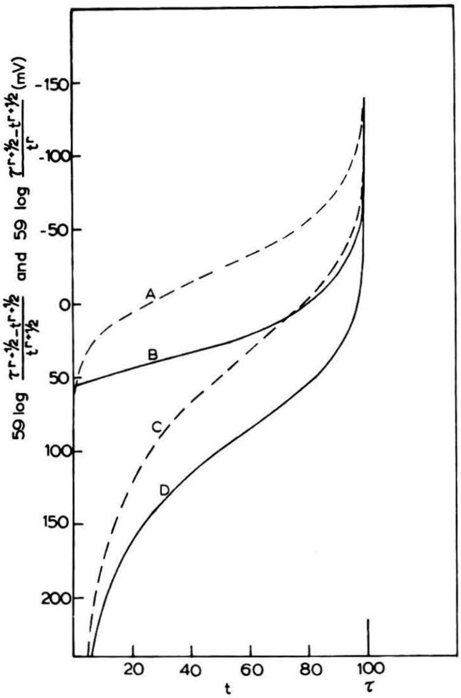


Fig. 4. Comparison of chronopotentiograms for reversible and irreversible electrode reactions: $\tau = 100$ sec; $T = 25°$; $n = 1 = \alpha n_A$; (A) reversible, $r = 0$; (B) irreversible, $r = 0$; (C) reversible, $r = 5/2$; (D) irreversible, $r = 5/2$.

ence in n and αn_A is taken into consideration. Fig. 4 presents a comparison of the calculated potential-time curves for a reversible and an irreversible electrode reaction, assuming $n = \alpha n_A$. Eqn. 38 also predicts that the transition time obtained is independent of the rate of electron transfer.

DISCUSSION

Comparison with existing equations

To help substantiate the validity of the derivations given above, of which eqn. 30 is the most general, a comparison will be made of the equations reported in the literature and eqn. 30 for specific values of r.

$r = 0$, *chronopotentiometry with constant current.* Eqn. 30, written for $r = 0$, yields at the transition time ($A(0,t) = 0$)

$$\left\{\sum_{m=1,2,}^{m} \tau_m\right\}^{1/2} = \frac{0.886F}{\beta} \sum_{m=1,2,}^{m} n_m D_m^{1/2} A_m^{\circ} \tag{39}$$

where β is the constant current density (A/cm^2). This equation is identical to that previously reported[4,15] and, as is well known, reduces to the SAND equation in the case of a single component.

$r = 1/2$, *chronopotentiometry with current varying with the square root of time.* Eqn. 30, under the condition that $r = 1/2$, reduces at the transition time to

$$\sum_{m=1,2,}^{m} \tau_m = \frac{1.128F}{\beta} \sum_{m=1,2,}^{m} n_m D_m^{1/2} A_m^{\circ} \tag{40}$$

where β is expressed in A/cm^2 sec$^{1/2}$. This equation is identical to that derived by HURWITZ AND GIERST[5,6,7].

$r = 1$, *chronopotentiometry with linear current scan.* Eqn. 30, in the case of $r = 1$, yields at the transition time

$$\left\{\sum_{m=1,2,}^{m} \tau_m\right\}^{3/2} = \frac{1.329F}{\beta} \sum_{m=1,2,}^{m} n_m D_m^{1/2} A_m^{\circ} \tag{41}$$

where β is expressed in A/cm^2 sec. Although this equation, in its general form, has not previously appeared in the literature, equations for a single species[8] and for two component mixtures[9] have been given. Eqn. 41 is identical to that given by these authors for such cases.

$r = -1/2$, *chronopotentiometry with current varying inversely with the square root of time* (*chronoamperometry*). Eqn. 30, under the condition that $r = -1/2$, gives for $A(0,t) = 0$

$$\left\{\sum_{m=1,2,}^{m} \tau_m\right\}^{0} = 1 = \frac{0.564F}{\beta} \sum_{m=1,2,}^{m} n_m D_m^{1/2} A_m^{\circ} \tag{42}$$

where β is expressed in A sec$^{1/2}$/cm^2. Thus, when one attempts to obtain a solution for the "transition time" in this case, a limiting case corresponding to chronoamperometry is obtained. This is more evident when one substitutes the value of β into eqn. 42, yielding

$$i = \frac{0.564F}{t^{1/2}} \sum_{m=1,2,}^{m} n_m D_m^{1/2} A_m^\circ \tag{43}$$

Although, to our knowledge, an equation for chronoamperometry in the case of multicomponent mixtures has not been reported in the literature, obviously eqn. 43 is of the correct form and, in the case of a single component, reduces to the well known COTTRELL equation. Further discussion of this special case is given below.

Potential–time relationships

It is of interest to now compare the form of the chronopotentiograms expected when current is scanned according to different powers of time, r. The potential–time relationship for reversible reactions has been given previously (see eqn. 34 above). The shapes of the chronopotentiograms for various values of r are given in Fig. 2. The chronopotentiogram is symmetrical when $r = 1/2$; at a time equal to one half the transition time, the potential is equal to the polarographic half-wave potential. For values of $r < 1/2$, the time at which the potential is equal to the polarographic half-wave potential is a smaller fraction of the transition time, while with $r > 1/2$, the effect is the reverse. Furthermore, the potential–time curves are skewed in opposite ways depending on whether r is greater or less than $1/2$. At high values of r, the transition time is more well defined.

For the special case of $r = -1/2$, we have a case identical to that of chronoamperometry. In this sense, it is amusing to note that chronoamperometry may be considered to be a limiting case of chronopotentiometry. It is also obvious that one might take the opposite viewpoint. The classification hinges on the *modus operandi* (*i.e.* whether one applies an $i(t)$ function or an $E(t)$ function). It is clear that identical results can be achieved by either of these two techniques upon the proper choice of the $i(t)$ or $E(t)$ function. Under these conditions the time and distance dependent concentrations, $A(x,t)$ and $B(x,t)$, are identical for the two techniques, and a Maxwell Demon in the solution would be unable to detect which of the two techniques was being employed. In order to derive the potential–time relationship for $r = -1/2$, the surface concentrations of A and B are established from eqns. 22 and 23 to give

$$A(0,t) = A^\circ - \frac{\beta\pi^{1/2}}{nFD_A^{1/2}} \tag{44}$$

$$B(0,t) = \frac{\beta\pi^{1/2}}{nFD_B^{1/2}} \tag{45}$$

The latter equation is written under the condition that the initial concentration of B is 0. Assuming a reversible electrode process, substitution of eqns. 44 and 45 into the NERNST equation yields

$$E = E^\circ + \frac{RT}{nF} \ln \frac{A^\circ - \dfrac{\beta\pi^{1/2}}{nFD_A^{1/2}}}{\dfrac{\beta\pi^{1/2}}{nFD_B^{1/2}}} \tag{46}$$

As can be seen from eqn. 46, the potential is independent of time, as must be true for chronoamperometry. Substituting the value of β(*i.e.* $it^{1/2}$) into eqn. 46 and solving for the current yields

$$i = \frac{nFD_A^{1/2}A^\circ}{\pi^{1/2}t^{1/2}}\left\{1 + \frac{nFD_A^{1/2}}{RTD_B^{1/2}}\,\mathrm{e}^{E-E^\circ}\right\}^{-1} \tag{47}$$

Eqn. 47 also indicates that a constant potential is obtained. The value of potential will depend upon β, which is given as

$$\beta = \frac{nFD_A^{1/2}A^\circ}{\pi^{1/2}}\left\{1 + \frac{nFD_A^{1/2}}{RTD_B^{1/2}}\,\mathrm{e}^{E-E^\circ}\right\}^{-1} \tag{48}$$

The value of β which yields the ordinary COTTRELL equation ($A(0,t) = 0$) is obtained at sufficiently negative potentials, a condition where the exponential term in eqn. 48 is negligible in comparison to one. Furthermore this is the maximum value permissible for β. Eqn. 47 is identical to that reported by DELAHAY[16].

The above case represents the situation where the oxidized and reduced species are soluble in solution or in the electrode material. The case where one of these species is insoluble, $B(0,t) = 1$, can be handled similarly. Thus

$$i = \frac{nFD_A^{1/2}}{\pi^{1/2}t^{1/2}}\left\{A^\circ - \frac{nF}{RT}\,\mathrm{e}^{E-E^\circ}\right\} \tag{49}$$

For cases where $r < -1/2$ (but not < -1 because of the earlier mathematical restrictions), the term t will appear in the denominator of eqn. 30; hence for small values of time these equations lose their physical significance. In practice it would be expected that the potential would be initially quite negative and scan towards positive values as time proceeds, approaching some limiting potential determined by the value of β. In the presence of several species, the chronopotentiogram will exhibit several transition times corresponding to the time when the concentration of the products at the electrode surface reach zero. These products are formed at early times but, due to the decreasing current and continual influx of the more easily reducible species, a time will be reached when the current can no longer support the reduction of all species present. At this time the more difficulty reduced species is no longer being formed; furthermore its concentration will then commence to be decreased through reoxidation by the more easily reducible species and eventually will reach zero, resulting in a potential break.

Comparison of chronopotentiometric methods based on different values of r

Concentration range. A continual problem in the use of constant current chronopotentiometry is the wide divergence in transition times obtained for reasonable spans of concentrations when a given constant current is employed. For example, selection of too small a current for analysis of an unknown solution may result in immeasurably long transition times. Often several trials at different current densities are required in order to secure an appropriate transition time for measurement. This difficulty can be circumvented by using a large value of r, since for such values, the range of transition times obtained for given concentration intervals is compressed. The data in Table II illustrate this point. It is seen that current varying with the square of time ($r = 2$) yields a reasonable range of transition times for concentrations varying by three orders of magnitude. While it is obvious that the use of $r = 2$ will not yield data as precise as obtained using small values of r, it will allow a sufficiently accurate estimate of the concentration so that a second experiment, using a lower r value, can then be performed under conditions designed to give an optimum value of transition time.

TABLE II

EFFECT OF r ON TRANSITION TIMES OBTAINED FOR A GIVEN CONCENTRATION RANGE

r	$\tau(A^\circ = 10^{-4}\ M)$[a] (sec)	$\tau(A^\circ = 10^{-1}\ M)$[a] (sec)
0	0.0730	73.000
1/2	0.344	344
1	0.574	57.4
2	0.763	12.1
3	0.861	6.19
4	0.922	4.23

[a] Assuming $\beta = 1.00 \cdot 10^{-4}$ A/cm² sec^r, $D = 1.00 \cdot 10^{-5}$, and $n = 1$.

The relative compression achieved by the use of a high r value, r_2, may be expressed as

$$\frac{\tau(A_1^\circ, r_1)}{\tau(A_2^\circ, r_1)} = \left\{\frac{\tau(A_1^\circ, r_2)}{\tau(A_2^\circ, r_2)}\right\}^{\frac{r_2+1/2}{r_1+1/2}} \tag{50}$$

where r_1 and r_2 refer to the two techniques respectively and the range of concentrations is from A_1° to A_2°. For example, in the case of chronopotentiometry with constant current ($r_1 = 0$) with a concentration range of three orders of magnitude, the range of the transition times obtained using a constant β varies by a factor of 10^6. Eqn. 50 may be used to evaluate the magnitude of r_2 which would yield a transition time range of 10 for the same concentration range. The calculated value of r_2 is found to be 2.5.

Of greatest analytical importance, however, is the relative error in estimating the concentration of the species. By differentiation, an expression of the relative error can be obtained from eqn. 22.

$$\frac{\mathrm{d}A}{A^\circ} = \left(\frac{r + 1/2}{\tau}\right)\mathrm{d}\tau \tag{51}$$

where $\mathrm{d}A/A^\circ$ is the relative error resulting from a given error in τ,($\mathrm{d}\tau$), and the term $(r + 1/2)/\tau$ is the error coefficient. Under the assumption that the error in estimating τ,($\mathrm{d}\tau$), is independent of the value of r and the concentration, the relative error is then readily estimated from the value of the error coefficient. The smallest relative error will be obtained at the lowest values of the error coefficient. Hence the most precise results are obtained when r is small and τ is large. Eqn. 51 is seen to be indeterminate for the limiting case of $r = -1/2$.

Effect of double layer capacitance. Thus far we have neglected the contribution of non-faradaic processes. It would, therefore, be of interest to compare the relative merits of the methods based on various values of r with respect to charging effects. The number of coulombs required to alter the potential of an electrode of capacitance C through a potential interval, E_1 to E_2, may be given by the following approximate expression

$$Q_c = C(E_1 - E_2) \tag{52}$$

(where the approximation arises from the assumption of a constant electrode capacitance). It would be of interest to compare this quantity with the number of coulombs employed for the faradaic process (in the absence of charging effects). The ratio of the number of coulombs required for the non-faradaic and faradaic processes as a function of time is

$$\frac{Q_c}{Q_f} = \frac{C(E_1 - E_t)(r+1)}{\beta t^{r+1}} \tag{53}$$

To obtain this ratio at the transition time, one may substitute eqn. 24 into eqn. 53 to obtain

$$\left(\frac{Q_c}{Q_f}\right)_{t=\tau} = \frac{C(E_1 - E_2)(r+1)\Gamma(r+1)}{nFD^{1/2}A^{\circ}\tau^{1/2}\Gamma(r+3/2)} \tag{54}$$

From eqn. 54, it may be deduced that the effect of charging is minimized at large concentrations. The evaluation of the terms containing r in eqn. 54 indicates that charging effects are minimized with low values of r. This is illustrated in Table III, although the effect is not large.

TABLE III

EFFECT OF r ON CHARGING ERRORS

r	$\frac{(r+1)\,\Gamma(r+1)}{\Gamma(r+3/2)}$[a]
0	1.13
1	1.50
2	1.81
3	2.06
4	2.29
5	2.50

[a] See eqn. 54.

The effect of charging on the shape of chronopotentiograms will vary according to the value of r and time. The ratio of non-faradaic to faradaic current

$$\frac{i_c}{i_f} = -\frac{C}{\beta t^r}\frac{\mathrm{d}E}{\mathrm{d}t} \tag{55}$$

is dependent upon the value of the rate of change of potential, $\mathrm{d}E/\mathrm{d}t$. This latter term may be evaluated for reversible electrode processes by differentiation of eqn. 34. This gives

$$\frac{i_c}{i_f} = \frac{CRT(r+1/2)}{\beta n F}\left(\frac{\tau^{r+1/2}}{t^{r+1}(\tau^{r+1/2} - t^{r+1/2})}\right) \tag{56}$$

Hence the fraction of the current consumed by charging the double layer, and thus the resulting distortion in the chronopotentiogram, is greatest at very low values of time and at values of time approaching the transition time, τ. This is to be expected since these are the very regions where $\mathrm{d}E/\mathrm{d}t$ is largest. As r increases, the ratio of these currents is relatively large at very small values of time but rapidly diminishes to a negligible value at higher values of time. For this reason there is little distortion in the chronopotentiogram in the vicinity of the transition time for higher values of r. It must be remembered, however, that the overall effect of increasing r is to increase total capacitance effects.

ACKNOWLEDGEMENT

This research was supported in part by a grant from Research Corporation.

SUMMARY

Current programming in chronopotentiometry has been extended to the use of current functions which vary with a power of time, $i = \beta t^r$. Equations have been derived for single and multicomponent mixtures. The equation for the transition time has the general form:

$$\tau^{r+1/2} = k_{(r)} A^\circ$$

where $k_{(r)}$ is a constant whose value depends on r and A° is the concentration of electroactive species. Chronoamperometry is found to be a special case arising when $r = -1/2$. Potential-time relationships for reversible and irreversible processes as a function of r are given. The effect of concentration range and double layer capacitance is also discussed.

REFERENCES

[1] T. Berzins and P. Delahay, *J. Am. Chem. Soc.*, 75 (1953) 4205.
[2] A. C. Testa and W. H. Reinmuth, *Anal. Chem.*, in the press.
[3] M. Senda, *Rev. Polarog. (Japan)*, 4 (1956) 89.
[4] T. Kambara and I. Tachi, *J. Phys. Chem.*, 61 (1957) 1405.
[5] H. Hurwitz and L. Gierst, *J. Electroanal. Chem.*, 2 (1961) 128.
[6] H. Hurwitz, *J. Electroanal. Chem.*, 2 (1961) 142.
[7] H. Hurwitz, *J. Electroanal. Chem.*, 2 (1961) 328.
[8] W. H. Reinmuth, *Anal. Chem.*, 32 (1960) 1509.
[9] R. C. Bowers, G. Ward, C. M. Wilson and D. D. DeFord, *J. Phys. Chem.*, 65 (1961) 672.
[10] O. Dračka, *Collect. Czechoslov. Chem. Communs.*, 25 (1960) 338.
[11] C. Furlani and G. Morpurgo, *J. Electroanal. Chem.*, 1 (1960) 351.
[12] R. M. King and C. N. Reilley, *J. Electroanal. Chem.*, 1 (1960) 434.
[13] A. C. Testa and W. H. Reinmuth, *Anal. Chem.*, 32 (1960) 1512.
[14] D. H. Geske, *J. Am. Chem. Soc.*, 81 (1959) 4145.
[15] C. N. Reilley, G. W. Everett and R. H. Johns, *Anal. Chem.*, 27 (1955) 483.
[16] P. Delahay, *New Instrumental Methods in Electrochemistry*, Interscience Publishers, New York, 1954.

Book Reviews

Temperature Measurement and Control, by W. F. COXON, Heywood and Co., Ltd., London, 1960, 312 pages, £3.

This book, part of the series entitled *Physical Processes in the Chemical Industry* has a fundamentally technological character, and is written with the aim of giving a clear and precise understanding of the field of measurement and control of temperature of technicians working in the chemical industry.

The volume begins, therefore, with a detailed description of the methods normally used for the measurement of temperature, and of the fundamental principles on which these methods are based.

In this section, which has a mainly descriptive character and is the most extensive, definitions are given of the ranges of measurement and the precision of the various apparatuses which are then fully described.

The second section deals with automatic control of temperature and the appropriate apparatus, along with an explanation of the various control systems (on-off, proportional, integral, derivative, etc.). The arguments are presented with a great deal of clarity so as to render them understandable even to those who are not specialists in this field.

The last chapters are dedicated to the practical applications which are most frequently encountered in industry. The examples are described in a rather general fashion, by means of simplified diagrams of installations of various types of control apparatus.

The work also presents a summary of the internationally used methods of calibrating the equipment.

The book also gives, in a clear and systematic if not very profound manner, the derivations inherent to the measurement and control of temperature, without however giving much detail as regards the mathematical formulation of the various theories.

The reading of this book, therefore, will be useful to those who wish to obtain a complete outline of the achievements in this field, while for the specialist in this subject, the book can only be considered as a useful summary.

R. FALINI, Istituto Superiore di Sanità, Rome

Microanalysis by the Ring Oven Technique, by H. WEISS, Pergamon Press, London, 1961, 112 pages, £1 10s.

The ring oven technique is a relatively new analytical tool, developed by Dr. WEISS in Vienna, which has proved to be very useful for the detection, and sometimes also for the semiquantitative evaluation, of components in one drop of solution. During the short length of time of about six years this new technique has become widely used in different laboratories so that this book, describing the principles of the method and the apparatus needed, schemes for the separation of cations and anions and also instructions for semiquantitative analysis, truly fills a gap, in the field of spot analysis.

The contents of this book are divided into four chapters: apparatus and its use; qualitative analysis including separation, systematic analysis and identification of ions; semiquantitative evaluation by means of spot colorimetry; and finally combination with other microtechniques.

Doubtless this new technique should be, as far as possible, known by all chemists concerned with the analysis of very small samples, and the clarity with which this book is written adds to its value.

The type setting and figures are very clear.

Methoden zur chemischen Analyse von Gummimischungen, 2nd. edn., by H. E. **Frey**, Springer Verlag, Berlin, 1960, VIII + 169 pages, 26 figures, D.M. 19.80.

This handbook has no scientific pretensions, since it aims to be only a quick and easy reference-guide for people concerned with the chemical analysis of rubber.

Its main value consists of its giving in a few pages, a clear description of all analytical methods of some practical importance. It is clear that in such a handbook, the most important thing is the critical choice of the methods. The author reports methods in use at his laboratory at the Standard Oil Co., Indiana, as well as in similar laboratories of other important rubber manufacturers. Several methods were taken from the ASTM or British Standards Institution, both of which are often mentioned in this book. At the end of each paragraph a bibilography is supplied. After the preface, the handbook is divided into four descriptive parts. The first part covers mineral fillers analysis, determination of total fillers, identification of the different types of fillers, and determination of sulfur in different types of carbon black.

The second part deals with the analysis of organic constituents: identification of the elastomer type and quantity in compounds, extractions with acetone, chloroform and alcoholic potash and determination of albuminoids, antioxidants and accelerators.

The third part deals with particular problems, such as the identification of linear polymers, efflorescence, the determination of trace noxious elements (copper and manganese), selenium and tellurium.

The fourth part by K. E. **Kress** of the Firestone Co. (given in English) refers to the application of absorption spectrometry as an analytical instrument in the rubber field.

It deals with the identification of antioxidants, accelerators, resins and softeners, black and mineral fillers, by means of absorption in ultra-violet and near infra-red, and identification and estimation of elastomers by analysis with salt — optics spectrometers in the range 3.2–14 μ.

The merits of the book — brevity and clearness — also establish its limits: matters are dealt with in an elementary way and people wishing to face problems with a critical mind may have to refer to different treatises; this does not however, reduce, its value for people concerned with routine tasks.

A. **Antonioli**, Laboratori Riuniti Studi e Ricerche (E.N.I.), San Donato Milanese

---

Analytical Chemistry of Polymers. Part 1. Analysis of Monomers and Polymeric Materials — Plastics — Resins — Rubbers — Fibers, Vol. 12, ed. G. M. **Kline**, Interscience Publishers Inc., New York, 1959, XVIII + 666 pages, $ 16.50.

G. M. **Kline** of the National Bureau of Standards is the editor of this book, written by 26 well-known specialists, working in top companies in the rubber and plastic fields in the United States and Canada, or in Universities or Institutes of Technology. Such authoritative contributions ensure the maximum of up-to-date information in the wide field covered by this book.

The text is divided into 20 chapters, sub-divided according to materials: acrylic plastics, alkyds, amino-resins, cellulose derivatives, epoxide resins, ethylene and fluoroethylene polymers, furan resins, natural resins, phenolic resins, polyamides, polyesters, proteins, rubbers (elastomers), silicones, styrene monomers and polymers, vinyl polymers and copolymers, ion exchange resins, plasticisers, synthetic and natural fibers, and drying oils.

For each of these materials the methods adopted in the leading American laboratories for the assay and determination of impurities in monomers are reported; this is followed by a discussion of the analytical problems involved in the identification and characterisation of the chemical compositions and physical properties of the polymers.

The book is not merely a collection of well-described methods of analysis since also the scope, theoretical principles and limitations of each method are discussed. The exposition is very functional: for the less common methods a detailed description of the working rules is given, whilst the standard or well-known ones are briefly described, with reference to original literature.

In this first part the different chemical and physical analytical operations are reported for the characterisation of monomers, polymers and auxiliary materials; a second part is planned to include molecular structure determinations, identification procedures for polymers and chemical group analysis.

The merit of this book is not confined to the high standard of the different chapters but also to the fact of having collected a great many procedures previously scattered through technical books and magazines on elastomers and plastics, and in the technical literature of the many industrial fields in which they find application: *e.g.* adhesives, paper, textile and protective coating industries.

A. **Antonioli**, Laboratori Riuniti Studi e Ricerche (E.N.I.), San Donato Milanese

Oszillographische Polarographie mit Wechselstrom, by J. Heyrovský and R. Kalvoda, Akademie-Verlag, Berlin, viii + 198 pages, 156 figures, D.M.21.

This long-awaited monograph, concerning the principles, experimental procedures and possibilities of the special technique of oscillographic polarography, is based on the experience gained in the last 20 years during its development and application by J. Heyrovský and his school. It is, in fact, a galvanostatic technique. An a.c. current of constant amplitude and frequency polarizes a dropping or a jet mercury electrode and the resulting voltage–time curve is recorded by an oscilloscope. The recording of the derivative dE/dt against the applied potential E is of even higher sensitivity. On an elliptical curve one gets cuts in the cathodic and anodic branches at the potentials at which a substance is reduced and oxidized. The depth depends on the concentration. After a chapter on general principles and theory (hitherto developed only approximately) general remarks on the study of electrode processes and the kinetics of the chemical reactions involved are given. As surface-active non-reducible or non-oxidizable substances also give characteristic cuts, by lowering the differential double-layer capacity in the potential range of their adsorption, the analytical applications are extensive and interesting possibilities for the investigation of problems of inhibition are offered. Characteristic criteria for the oscillograms for different types of electrode processes are summarized.

The apparatus section is very instructive. Detailed circuit diagrams with all the data for the elements used enable the reader to build every necessary circuit as long as an oscilloscope is available to him. Also the performances of the several types of "polaroscope" designed especially for this method by Heyrovský and manufactured by "KOVO", Prague, are discussed in detail. This instrument includes some auxiliary equipment, such as a unit for controlling drop-time by knocking off the drops; a compensator for the ohmic drop in solution, etc. Other circuits, such as those for applying current at predetermined intervals of drop-time or for working with single a.c. pulses per drop may be constructed according to the descriptions given.

The second half of the book deals with the general experimental performance of the different electrode types and the evaluation of the oscillograms mentioned in the introduction. A detailed discussion of all important previous investigations of substances in inorganic and organic chemistry, pharmacy and medicine with many original oscillograms follows. This section will certainly stimulate further research to a large extent. A great help in this connection will be the excellent literature index (172 references) at the end of the book.

The main advantage of the method seems to be its rapidity and experimental simplicity. Its main fields of application are therefore the purity control of products, rapid semi-quantitative analysis and fundamental studies on the course of electrode processes. For the latter the short time needed for measurement and the possibility of frequently obtaining both cuts (cathodic and anodic) of a substance is of great importance. But by using more improved and complicated circuits exact quantitative determinations, microanalysis and several titration methods are also possible as is shown. On the whole the book deals mainly with practical problems and experimental procedures and one may hope that it will stimulate many chemists to apply this simple and rapid method with all its striking possibilities to their problems over a much wider range than is done at present.

For a new edition, more detailed, clearer and better discussion of the theoretical principles seems very desirable.

H. W. Nürnberg, Max-Planck-Institut für Eisenforschung, Düsseldorf

J. Electroanal. Chem., 3 (1962) 80

The Encyclopaedia of Spectroscopy, edited by George L. Clark, Reinhold Publishing Co., New York, 1960, xvi + 787 pages, $25.

Vor 30 Jahren war es noch möglich, die Spektroskopie in ihrer Gesamtheit zu beherrschen. Heute nicht mehr. Und doch muss auch ein Spezialist wenigstens die Nachbargebiete kennen, denn oft sieht man sich in seinem Teilgebiet vor einer Grenze, die mit Hilfe einer anderen Nachweismethode umgangen oder hinausgeschoben werden kann.

Darum ist es ein dankenswertes und fruchtbares Unternehmen, ein ganzes Gebiet von Untersuchungsmethoden zusammenzufassen, wie dies in dem vorliegenden Werk für die Spektroskopie geschehen ist.

Die 23 wichtigsten Arten der Spektroskopie — neben den traditionellen Arten seien hier nur genannt β-, γ-, Neutronen-, N.M.R., Mikrowellen-Spektroskopie — bilden alphabetisch geordnet die Hauptkapitel des Buches, und unter jedem dieser Titel werden in einzelnen Artikeln verschiedene dazugehörige Aspekte behandelt, wie Geschichte, Theorie, Instrumentation, Verfahren, Auswertung und Anwendungen, sodass das ganze Thema erschöpfend erfasst wird, soweit dies natürlich in einem einzigen Band, von allerdings 780 Seiten, möglich ist.

Die einzelnen Beiträge sind von namhaften Fachleuten (160 an der Zahl) der betreffenden Gebiete geschrieben, wobei gelegentlich anfallende Lücken vom Herausgeber selbst aufgefüllt werden. Natürlich wäre es von Vorteil, und das hat der Herausgeber selbst gefühlt, wenn ein einziger Autor, oder wenigstens eine kleine Gruppe den ganzen Stoff behandelt hätte, im Hinblick auf einen gleichförmigen Stil, Vermeidung von Überschneidungen, Wiederholungen und Lücken. Doch ist dies praktisch kaum möglich. Man bedenke nur die Unzahl der Anwendungsgebiete der 23 Arten von Spektroskopie: Chemie, Physik, Biologie, Medizin, Metallurgie, Geologie, Mineralogie, Elektronik, chemische und pharmazeutische Industrie, usw.

Die Darstellung ist durchwegs leicht verständlich gehalten, bietet aber in aller Kürze eine Fülle von theoretischem und praktischem Material und Angabe der wichtigsten Literatur. Druck, Illustrationen und die ganze Aufmachung sind mit grosser Sorgfalt vorgenommen worden. Ein ausführliches, leider fehlendes, Sachregister würde die Nützlichkeit des Werkes noch bedeutend erhöhen.

E. SALPETER S.J., Vatican Astronomical Observatory, Castel Gandolfo, Rome

J. Electroanal. Chem., 3 (1962) 80–81

Physiko-chemische Grundlagen und Tabellen zur qualitativen Analyse, von W. D. TREADWELL, O. GÜBELI UND W. PRODINGER, Verlag Franz Deuticke, Wien, 1960, xii + 236 Seiten, Austr. Schill. 168.

Im täglichen Gebrauch, die Hilfe eines guten Tabellenwerkes für die Ausführung der normalen qualitativen Analyse ist sehr bequem. Die jetzt neubearbeiten Tabellen von W. D. TREADWELL (von O. GÜBELI UND W. PRODINGER herausgegeben) stellen die letzte wissenschaftliche Lehrtätigkeit dieses grossen Meisters der analytischen Chemie, der die Neubearbeitung dieses Tabellenwerkes noch kurz bevor seines Todes zu Ende bringen konnte.

Die Tabellen sind in sechs Abschnitten geteilt: (I) Physikalisch-chemische Grundlagen, Definitionen und Tabellen mit vielen für die praktische Durchführung der qualitativen Analysen wichtigen Zahlenangaben; (II) Allgemeine Übersicht und analytisches Verhalten der häufigeren Kationen; (III) Allgemeine Übersicht und analytisches Verhalten der meisten anorganischen (und von fünf der wichtigsten organischen) Säuren; (IV) Reaktionen auf trockenem Wege; (V) Gang der Analyse (meistens in Tabellenform); (VI) Allgemeine Übersicht und analytisches Verhalten der selteneren Elemente (unter Berücksichtigung auch physikalischer Methoden).

Das ganze Werk kann als ein guter praktischer Führer der altbekannten klassischen quantitativen Analyse angesehen werden, die heute noch immer grosse Dienste leisten kann.

Für spätere Ausgaben könnten vielleicht einige Verbesserungen vorgeschlagen werden, wie, z.B., die Angabe der Elektrodenspannungen nach der sogenannten ,,Europäische Vorzeichen-Konvention" (die allmählich auch von einigen der besten Amerikanischen Lehrbüchern angenommen wird); die Angabe der Erfassungsgrenze für alle vorgeschlagenen analytischen Reaktionen und vielleicht ein Abschnitt über die Reinheitsprüfung, d.h. Spurenanalyse in Anwesenheit eines sehr grossen Überschusses anderer Stoffe.

J. Electroanal. Chem., 3 (1962) 81

Komplexometrie, Band I, Prinzipien und Grundbestimmungen, par R. PŘIBIL, Deutscher Verlag für Grundstoffindustrie, Leipzig, 1960, 150 pages, D.M. 12.

Le Dr. PŘIBIL a fait de très nombreux travaux dans le domaine des complexes, aussi était il particulièrement qualifié pour traiter un pareil sujet dont l'importance ne cesse de croître.

Le premier volume de cet ouvrage est de dimension modeste. Fort bien fait, parfaitement ordonné, les exposés y sont clairs et dépouillés de toute littérature inutile. Après un très court historique, l'auteur présente, en quelques pages et de façon très simple, les bases théoriques. Il est question des constantes des couples acide–base et de la stabilité des complexes que forme l'EDTA avec les métaux. Cet exposé est suivi d'un chapitre sur les indicateurs métalliques (éroit, murexide,

J. Electroanal. Chem., 3 (1962) 81–82

thorin, chromazuol . . .) qui sont classés d'après leur groupement caractéristique et dont l'auteur donne la formule et les propriétés essentielles.

Quelques renseignements concernant la technique opératoire précèdent les dosages complexométriques des solutions de métaux purs et de mélanges de ceux-ci. Le délicat problème de la sélectivité et du masquage est traité avec quelques détails ainsi que les applications de la complexométrie aux méthodes physico-chimiques (ampérométrie, potentiométrie, photométrie . . .).

Bien que le papier ne soit pas de première qualité, le livre est agréable à consulter car l'impression y est claire et le texte intelligemment disposé.

Une bibliographie qui paraît judicieusement choisie et une table des matières succinte mais bien conçue termine cet ouvrage que nous nous faisons un plaisir de recommander.

D. MONNIER, Université de Genève

Michael Faraday. A list of his lectures and published writings, by ALAN E. JEFFREYS, Chapman and Hall Limited, London, 1960, xxviii + 86 pages, £2 2s.

This book aims at recording in chronological order the published writings and lectures of Michael Faraday. It lists all books and separate publications, including later editions and reprints, all letters, papers and articles in journals and periodicals, and letters to "The Times". All lectures, whether they have appeared in print or not, and all manuscript notes in the Faraday collection of the Royal Institution have been included. It is restricted to material published in English in Great Britain, so that translations and American publications of works already published in Great Britain are excluded. Most personal letters have also been omitted.

In the course of a lengthy introduction the author has classified his material under a large number of headings and has included many interesting and instructive details. Sources of information are fully dealt with and the methods by which unsigned articles etc. have been ascribed to Faraday are discussed in detail. Useful sections deal with the material not included in this book and with the arrangement of the entries.

It is surprising to find that, in spite of the numerous biographies of MICHAEL FARADAY, no comprehensive bilbiography (save that of LUKOMSKAYA in the U.S.S.R.) has been attempted. This book remedies this signal omission. It is obviously meant to be a work of reference for students and research workers and is not intended to be readable. Nevertheless, as Sir LAWRENCE BRAGG says in his Foreword, the bare record of Faraday's writings year by year is in itself fascinating, and since it includes even sermons and Parliamentary papers on a wide variety of subjects, it shows the breadth of his interests.

The book has good clear type and is printed on substantial paper. The illustrations are well chosen. It is well laid out and has a detailed index and list of biographies of Faraday. It forms a valuable addition to any reference library and could well be taken as an example of how such surveys should be presented.

G. F. REYNOLDS, Ministry of Aviation, Woolwich

La Spectroscopie Hertzienne Appliquée à la Chimie, by R. FREYMANN AND M. S. SOUTIF, Dunod, Paris, 1960, xi + 263 pages, N.Fr. 23.

This book, relating to a number of conferences attended by the authors some years ago, is primarily intended for the French reader, since the authors themselves in the Introduction complain of the poor knowledge of these chemico-physical methods in France. However it can be read with great advantage by physicists and chemists in any country, as it contains a brief, but sufficiently complete summary of the current theories and applications of the following modern instrumental techniques.

(1) Absorption by molecular rotation (microwave spectroscopy) — 10 pages. A very brief account is given of the theory and experimental technique, followed by a list of chemical substances, the rotational spectra of which have already been determined.

(2) Dipolar Debye Absorption (D.D.A.: measurement of the complex dielectric constant as a

function of frequency and of temperature) — 49 pages. The simple determination of electric dipole moments is not included in this section. The importance of D.D.A. in solid state physics is stressed and a long account is given of its applications.

(3) Nuclear Paramagnetic Resonance (N.M.R.) — 81 pages. The enormous amount of material collected in the last few years in this field makes its subdivision difficult. A large number of representative examples are discussed here, and grouped under the different techniques available.

(4) Electronic Paramagnetic Resonance (E.P.R.) — 78 pages. The field of application of this technique is less general than that of N.M.R., since it is limited to molecules in which unpaired electrons are present, but its importance is nevertheless increasing, and is suitably stressed here. A general outline (theories, techniques, applications) follows. At the end, a brief account is given of the double resonance methods; OVERHAUSER effect, ABRAGAM effect; and FEHER method.

(5) Finally, a brief introduction is given to Quadrupolar Nuclear Resonance and its still limited chemical applications are discussed.

A general description of these five phenomena and a short summary of the common principles and techniques involved are given at the beginning.

Details such as the choice of symbols and the figures seem to be of a high standard. At the end of each chapter satisfactory lists of books and of fundamental papers enable the interested reader to extend his knowledge of the subject.

G. NENCINI, Laboratori Riuniti Studi e Ricerche (E.N.I.), San Donato Milanese

J. Electroanal. Chem., 3 (1962) 82–83

Flammenspektralanalyse: Grundlagen und Verfahren der Flammenphotometrie und Flammenspektrographie, by W. SCHUHKNECHT, F. Enke Verlag, Stuttgart, 1960, xii + 258 pages, D.M. 69.

The author in his approach to the subject is essentially methodical and descriptive. One third of the book is devoted to analytical methods which deal, almost entirely, with alkali metals and alkaline earth elements.

In comparison with other recently published treatises, this book gives an extensive description and criticism of the different types of atomizers and burners. The author himself started to use a filter photometer in 1936 for the determination of potassium, the same type of photometer being still in use to-day for the analysis of soils and fertilizers.

The author emphasizes the difference between simple flame photometry and flame spectrophotometry: in the first process filters are used and in the second prisms or grating monochromators. In the description he distinguishes between the use of photometers and spectrophotometers.

Only a few pages refer to flame spectrography, these dealing with the use of a photographic emulsion. No mention is made of flame absorption spectroscopy, the analytical applications of which date back to 1955. Recording instruments are not described.

The book contains extensive references which are divided into fixed periods beginning in 1859 with BUNSEN's first paper. The author, a pioneer in flame spectral analysis, has made a rich contribution in this book to the better understanding of the difficulties of flame spectral analysis, the applications of which have often been misconceived.

R. INTONTI, Istituto Superiore di Sanità, Rome

J. Electroanal. Chem., 3 (1962) 83

Bibliografia Polarografica, (1951–59) Part I, Supplement No. 12, by L. GRIGGIO, Supplement to *Ricerca Scientifica*, 30 (1960); 80 pages, lire 1000.

This is the twelfth supplement to the well-known *Polarographic Bibliography* initiated by G. SEMERANO and edited as a special publication of the Italian Consiglio Nazionale delle Ricerche, which lists all polarographic papers which have appeared in the chemical literature, arranged for every year, according to the alphabetical order of the authors, and quoting the name of the author, place and date of appearance, and either the original title or its English translation. The twelfth supplement contains some few addenda to the references of the years 1951 to 1956 and an extensive list of papers published in 1957, 1958 and 1959, with a total of about 1000 references.

C. FURLANI, University of Rome

J. Electroanal. Chem., 3 (1962) 83

Mass Spectrometry and its Applications to Organic Chemistry, J. H. BEYNON, Elsevier Publishing Co., Amsterdam, 1960, xii + 640 pages, £ 6.0.0, Dfl. 63.00.

The lay-out of this new book on mass spectrometry differs considerably from the existing texts on this subject and mainly concerns its applications to organic chemistry.

The first part of the book is devoted to the description of the instrument and to some instrumental techniques. This instrumental part is written for the user and not for the maker of the apparatus; it gives many original examples of applications to chemical problems and it contains every topic the mass spectrometrist is supposed to know in order to understand his instrument.

The importance of the sampling problem in mass spectrometry (as in many chemico-physical techniques) is stressed by the author who devotes 66 pages to this topic. These pages, full of simple illustrative designs may be profitably consulted by experts as well as by beginners.

But the core of the book is formed by the successive 245 pages which are devoted to mass spectra and their interpretation. This part is largely unique, as it contains the results of years of research and analytical work in the author's own laboratory at the I.C.I. Dyestuffs Division in Manchester.

Mass spectrometry has just gained its place among the other spectrometric techniques in the qualitative analysis of organic compounds, and this part of the book can parallel L. J. BELLAMY's manual on the infra-red spectra of complex molecules.

Correlations of spectra of many classes of organic compounds are given, ranging from hydrocarbons to molecules containing O, N, S, Si, halogens, and other atoms. Particular care is given to some typical aspects of spectra such as metastable ions, recombination ions and ions with initial kinetic energy. A chapter on other applications of mass spectrometry follows the more conventional line of other books on the subject.

At the end of the book, 100 pages of appendices give a number of valuable original tables calculated mainly in the author's laboratory. Among others we can mention the masses and isotopic abundance ratios for various combinations of C, N, H and O atoms, and the nomograms for the determination of the origin of metastable ions.

A list of 2213 references concludes this book which may certainly be considered an important step in the progress of mass spectrometry as an analytical tool.

G. NENCINI, Laboratori Riuniti Studi e Ricerche (E.N.I.), San Donato Milanese

---

Advances in Polarography, by I. S. LONGMUIR, Symposium Publications Division, Pergamon Press, London, 1960, in 3 vols: Vol. I xv + 407 pages, Vol. II ix + 396 pages, Vol. III vii + 401 pages; £15 per set.

These three volumes contain the Proceedings of the Second International Congress of Polarography, which was held at Cambridge in 1959, and which was attended by the most authoritative exponents of this branch of electrochemistry, including J. HEYROVSKÝ, the initiator of the polarographic technique and recent Nobel Prize winner. The book gives a fairly complete survey of the state and of the trends in the development of polarography at the time of the Congress, since it contains contributions from all the most representative polarographic schools, covering nearly all the problems related to polarography, such as the theory of diffusive phenomena, polarographic behaviour of inorganic and of organic substances and their relationship to molecular structure, and analytical, biological and medical applications. Special attention is given to instrumental problems and to the development of new techniques of oscillographic, differential and a.c. polarography. Only the plenary lectures of the Conference are held at a level of informative description of the basic principles of polarography, and most of the papers contributed are specialized and are likely to be read only with difficulty by non-experts in polarography. No sharp division of arguments is effected among the three volumes, but, as a general trend, the first volume is devoted to general, theoretical and instrumental problems, the second one to inorganic and analytical polarography, and the third one to the behaviour of organic substances and to biological and medical applications. Most of the articles are in English, and only a few in German and in French.

C. FURLANI, University of Rome

ABSTRACTS SECTION

of the

JOURNAL
of
ELECTROANALYTICAL CHEMISTRY

Vol. 3 (1962)

EDITOR:
G. MILAZZO (Rome)

ELSEVIER PUBLISHING COMPANY
AMSTERDAM

Printed in The Netherlands by
Nederlandse Boekdruk Inrichting N.V.

1. Fundamental electrochemistry

1 – Electrochemical, electric and chemical tensions of cells and electrodes. P. Van Rysselberghe (Dept. of Chem. and Chem. Eng., Stanford University, Calif., U.S.A.). *Electrochim. Acta*, 3 (1961) 257–263.
The terms and presentation of the C.I.T.C.E. report on "Electrochemical Nomenclature and Definitions" are used in an analysis of galvanic cells which starts with chemically identical terminals and works gradually towards single electrodes in a manner submitted as suitable for text-book presentation. The various tensions are discussed and examined in relation to the so-called "European" and "American" conventions. [Author]

2 – Mixture potentials: the systems ferricyanide–ferrocyanide and iodine–iodide at platinum electrodes. M. Spiro, R. R. M. Johnston and E. S. Wagner (Chem. Dept., University of Melbourne, Australia). *Electrochim. Acta*, 3 (1961) 264–269.
Mixture potentials were measured at platinum electrodes using the two redox couples ferricyanide–ferrocyanide and iodine–iodide in water at 25°. The results are independent of the speed of stirring and of the size and treatment of the electrodes. The potentials developed on mixing can be quantitatively explained if the redox couples reach equilibrium rapidly at the platinum surface but not in the bulk of the solution. Other evidence supports this conclusion. The use of e.m.f. measurements for detecting heterogeneous catalysis in solution is discussed briefly. [Author]

3 – Organic semiconductors. II. The electrical resistivity of organic molecular complexes. M. M. Labes, R. Sehr and M. Bose (The Franklin Institute, Laboratories for Research and Development, Philadelphia 3, Pa., U.S.A.). *J. Chem. Phys.*, 33 (1960) 868–872.
Thirty molecular complexes, either electron acceptors or electron donors, were prepared and the electrical resistivities measured on compressed microcrystalline material. It was observed that a lowering of electrical resistivity is generally associated with complex formation. In the light of the observations, other results involving measurements of a small number of compounds with a given electron acceptor must not be considered as necessarily describing that class of complexes. The crystal structure is of great importance and may profoundly influence the electrical properties. [G.Mar.]

4 – Transport processes in liquid alloys. II. The electrical force on an ion. Paul G. Mangelsdorf, Jr. (Institute for the Study of Metals, University of Chicago, Ill., U.S.A.). *J. Chem. Phys.*, 33 (1960) 1151–1161.
In the present paper an attempt is made to justify Skaupy's theory and to give a correct quantitative expression using a minimum of assumptions. The Author examines the actual forces which are at work in causing the migration of the impurity ions. A dynamical model is proposed and electrons are treated as a quantum fluid. There is a force related to the fractional conductivity increment produced by a solute ion. The total force is directly proportional to this increment, to the field strength and to the average "free" charge of the average solvent ion.
The result is only exact in infinitely dilute solutions and cannot be expected to be even qualitatively true in solutions concentrated enough for solute–solute interactions to become important. The effective number of free electrons in pure liquid mercury is estimated to be 0.3 per atom. [G.Mar.]

5 – Theory of the diffuse double layer. F. H. Stillinger, Jr. and J. G. Kirkwood (Sterling Chemistry Laboratory, Yale University, New Haven, Conn., U.S.A.). *J. Chem. Phys.*, 33 (1960) 1282–1290.
The viewpoint adopted involves the determination of local ion densities in the double-layer region from the well developed fundamental theory of molecular distribution functions. The electrolyte is regarded as consisting of charged rigid spheres, suspended in a dielectric continuum, in which a planar, uniformly charged, electrode produces the double layer.
For sufficiently large dilutions, the usual linear Poisson–Boltzmann result is verified; at higher concentrations, the short-range ion–ion repulsions tend to set up a local lattice-like structure with alternating layers of positive and negative charge. Numerical computations for the reduced ζ potential clearly reflect the ionic ordering at distances further from the electrode than would be predicted by the linear Poisson–Boltzmann theory. [G.Mar.]

6 – **Diffusion of weak electrolytes.** W. H. Stockmayer (Dept. of Chem., Mass Inst. Technol., Cambridge 39, Mass., U.S.A.). *J. Chem. Phys.*, 33 (1960) 1291–1292.
An expression is obtained for the diffusion of a weak electrolyte. The restrictions are firstly that the solute can be treated as a single component, which excludes acid salts such as $KHSO_4$ or salts which hydrolyze extensively and secondly that the rates of all the chemical reactions are sufficiently rapid.
The result reduces to a simple form if all the mobilities are independent of concentration. The application to real solutions containing more than two ion species involves all the difficulties of the relaxation effect. [G.Mar.]

7 – **Studies of electrical tensions in non-aqueous binary systems. II. Studies of piperidine–allylic mustard oil and diethylamine–allylic mustard oil** (in Russian). F. N. Kozlenko and S. P. Miskidzhyan (Medical Institute, Lvov, U.S.S.R.). *Zhur. Fiz. Khim.*, 35 (1961) 26–30.
The binary systems piperidine–allylic mustard oil and diethylamine–allylic mustard oil both in the pure state and in the presence of a third component, 90% ethanol, have been investigated with the aid of a hydrogen and glass electrode. In all cases tension–composition curves were obtained corresponding in shape to the curves of the potentiometric titration curves of acids with bases, this suggesting an acido-basic character for the interaction between the components. It has been shown that such an interaction is in agreement with Lewis's theory of acids and bases. [Ot.So.]

8 – **Structural effects on the electrochemical reduction mechanism of organic compounds.** P. J. Elving (University of Michigan, Ann Arbor, U.S.A.). *Ricerca sci.*, (Suppl. No. 5, Contributi di Polarografia) 30 (1960) 205–215.
Theoretical considerations and experimental factors are discussed in order to explain the mechanism of an organic electrode reaction. Ionic substitution and free radical reactions are discussed and electrochemical carbon–halogen bond fission processes considered. The role of structural changes in the electroactive substance is emphasized as well as the importance of the structure in causing steric hindrance, in the steric control of products and in stereospecific electrode reactions. [Fr.Pan.]

9 – **Thermodynamics and conductance of simple electrolytes in polar organic solvents.** G. J. Janz (Rensselaer Polytechnic Institute, Troy, N.Y., U.S.A.). *Rensselaer Polytech. Inst. Progr. Rept. No. 4*, (1960) 11 pp; *Nuclear Sci. Abstr.*, 15 (1961) 176, abstr. No. 1321. [Ed.]

10 – **Fused salts.** G. E. Blomgren and E. R. Van Artsdalem (Union Carbide Corp., Parma, Ohio, U.S.A.). *Ann. Rev. Phys. Chem.*, 11 (1960) 273–306.
A review. [Ed.]

11 – **Thermodynamics of thermocells with fused or solid electrolytes.** Kenneth S. Pitzer (Dept. of Chem. and Lawrence Radiation Laboratory, University of California, Berkeley 4, Calif., U.S.A.). *J. Phys. Chem.*, 65 (1961) 147–150.
The thermodynamic principles related to thermocells are reviewed. The total "transported entropy" of the ionic species reacting at the electrodes is obtained for several cells. The transported entropy of metal ions in fused salts is approximately equal to estimated values of the partial molal entropies of these ions, hence the entropies of transfer are small. In solid electrolytes the entropies of transfer are sometimes large, and are discussed in terms of probable conductance mechanisms. [D.S.Ru.]

12 – **The free energy, entropy and enthalpy of transfer of sodium and potassium chloride from methanol to water and from ethylene glycol to water.** James K. Gladden and James C. Fanning (School of Chem., Georgia Institute of Technology, Atlanta, Ga, U.S.A.). *J. Phys. Chem.*, 65 (1961) 76–80.
The thermodynamic quantities of transfer were measured at three temperatures using the cell: Ag, AgCl | MCl(non-aqueous solvent) || $M(Hg_x)$ || MCl(water) | AgCl, Ag. The "limiting law" for the transfer process was expressed as a function of $N^{1/2}$. The deviations between the experimental values of the free energy of transfer and those calculated by use of the Born theory are best explained by considering the order–disorder producing nature of the solute's ions on the solvent. The order–disorder nature of ions can be described by use of the entropy of transfer. [D.S.Ru.]

13 – **The interpretation of polarographic current–voltage curves for irreversible electrode reactions.** J. E. B. Randles (Dept. of Chem., University of Birmingham, U.S.A.). *Contributi di Polarografia, suppl. Ricerca sci.*, 5 (1960) 191–203.
Fundamental considerations are summarized for the polarographic curves of kinetic electrochemical

processes. The current–time curve during one drop life and the current–voltage dependence may be used to distinguish between a slow chemical step and a slow electrode reaction as the rate-controlling step of the overall process. From these curves the kinetic parameters of a slow electrode reaction can be calculated, chiefly when a complete anodic–cathodic curve is obtainable.
[Fr.Pan.]

14 – The effect of migration on polarographic current (in Japanese). Shinzo Okada, Shiro Yoshizawa, Fumio Hine and Kameo Asada (Dept. of Ind. Chem., Kyoto University, Kyoto, Japan). *J. Electrochem. Soc. Japan*, 27 (1959) 140–143.
The equations of the polarographic limiting current which are applicable for any addition of indifferent electrolyte, up to the case of no indifferent electrolyte being present, were derived theoretically. The curvature of the mercury drop was ignored. Good agreement was obtained between the calculated and observed values of the limiting currents with the two systems: $Tl^+–Cl^-–K^+$ and $Pb^{2+}–Cl^-–K^+$. [Ta.Fu.]

15 – The progress of redox-reactions at metals and semiconductors. I. General remarks on electronic transfer between solid state and redox electrolyte (in German). H. Gerischer (Max-Planck-Institut f. Metallforschung, Stuttgart, Deutschland). *Z. physik. Chem. (Frankfurt)*, 26 (1960) 223–247.
Der Elektronenübergang zwischen einer Festkörperelektrode und einem gelösten Redoxsystem ($M^{z+1}aq\,/\,M^{z+}aq$) erfolgt durch Tunneleffekt von einem besetzten Quantenzustand des Festkörpers auf einen unbesetzten gleicher potentieller Energie im Elektrolyten bzw. umgekehrt. Eine neuartige grundlegende Theorie der Elektrodenprozesse wird auf dieser Basis entwickelt. Die Zahl der Elektronenübergänge pro Zeiteinheit hängt von der Anzahl besetzter und unbesetzter Energieterme gleicher Energie im Festkörper und Elektrolyten ab. Nur zwischen solchen sind Elektronenübergänge möglich. Die $M^{z+}aq$-Ionen entsprechen den unbesetzten und die $M^{z+1}aq$-Ionen den besetzten Termen im Elektrolyt. Die Lage der Terme fluktuiert hier entsprechend der thermischen Fluktuation der Solvathülle. Die Verteilungsfunktion der Terme ist im Elektrolyt ebenso wie im Festkörper eine Fermifunktion. Die kathodischen bzw. anodischen Teilströme sind dem Produk° aus der Zahl der besetzten Terme im Festkörper, und der Zustandsdichte der unbesetzten Terme im Elektrolyt (oxydierte Form) bzw. dem Produkt aus der Zahl der unbesetzten terme im Festkörper und der Zustandsdichte der besetzten Terme (reduzierte Form) im Elektrolyt proportional. Als weitere Faktor tritt ein vom jeweiligen Energiebetrag abhängiger Frequenzfaktor auf, der die für den betrachteten Elektronenübergang richtige Richtung des Anlaufens der Elektronen berücksichtigt und ausserdem die Durchtunnelungswahrscheinlichkeit enthält, sowie die geometrischen Eigenschaften der Elektrode. Konzentrationspolarisation wird ausgeschlossen. Für die zu einer bestimmten kinetischen Energie der Elektronen gehörende Übergangsfrequenz wird mittels eines einfachen Potentialkastenmodells eine einfache quantenmechanische Modellrechnung angegeben. [H.W.Nür.]

16 – The progress of redox reactions at metals and semiconductors. II. Metal electrodes (in German). H. Gerischer (Max-Planck-Institut f. Metallforschung, Stuttgart, Deutschland). *Z. physik. Chem. (Frankfurt)*, 26 (1960) 325–338.
Die im Teil I abgeleiteten allgemeinen Zusammenhänge werden auf Durchtrittsreaktionen an Metallelektroden angewandt. Alle Elektronenterme im Metall sowie das Ferminiveau dort sind entsprechend der Galvanispannung $\Delta\varphi$ infolge Aufladung um —$e_0{}^{\Delta\varphi}$ verschoben. Die Höhe der Potentialschwelle (in gröbster Näherung Rechteckschwelle) für den Elektronenübergang hängt vom Energieniveau ab auf dem der Elektronenübergang erfolgt, d.h. im wesentlichen von der Solvatstruktur des Redoxions. Die Austauschstromdichte entspricht dem Integral über das Produkt aus den Zustandsdichten der Elektronenterme im Metall und Elektrolyt und den entsprechenden Fermiverteilungsfunktionen der Elektronen in beiden Phasen. (Proportionalitätsfaktor ist die Übergangsfrequenz ν der Elektronen durch die Potentialschwelle.) Der Elektronenaustausch findet überwiegend in nächster Umgebung des Ferminiveaus statt. (Intervall von ± 0.25 eV bei 25° und Durchtrittsfaktor $\alpha = 0.5$.) Er hängt also entscheidend von den hier herrschenden Zustandsdichten der Elektronenterme ab. Die Unterschiede in ν und der Zustandsdichte im Metall sind für die verschiedenen Metalle gering, während die Zustandsdichte der Terme im Elektrolyt stark von den Verteilungsfunktionen der Solvathüllenzustände der beiden Redoxpartner abhängt. In dieser chem. Aktivierung, d.h. in der Häufigkeit der einen Elektronenübergang beim Ferminiveau begünstigenden Energiezustände der Solvathülle liegen die wesentlichen Unterschiede im Betrag der Austauschstromdichte für die verschiedenen Redoxsysteme. (Der Durchtrittsfaktor α ist nur in 1. Näherung konzentrationsunabhängig). Polarisation verschiebt das Ferminiveau des Metalles entsprechend weiter, so dass der anodische oder kathodische Teilstrom überwiegt. Erst bei so grosser Polarisation, dass das Ferminiveau des Metalles eines der Maxima der Zustandsdichte der Elektronenterme der Elektrolytkomponenten überschreitet, bestimmt deren Lage den Energiebereich des Elektronenüberganges, der dann praktisch nur noch in kathodischer bzw.

anodischer Richtung erfolgt. α ist bei grösseren Überspannungen nicht konstant, sondern eine Funktion der Überspannung(!), ein Umstand, der bei künftigen Studien von Durchtrittsreaktionen besonders beachtet werden muss. [H.W.Nür.]

17 – The progress of redox reactions at metals and semiconductors. III. Semiconductor electrodes (in German). H. Gerischer (Max-Planck-Institut f. Metallforschung, Stuttgart, Deutschland). *Z. physik. Chem. (Frankfurt)*, 27 (1961) 48–79.
Die im Teil I. entwickelten grundlegenden Ansätze werden auf die Durchtrittsreaktion beim System Halbleiter/Elektrolyt angewandt, unter Berücksichtigung der besonderen Eigenschaften der Halbleiter. Zwischen Elektronenübergängen in das Leit-bzw. Valenzband ist zu unterscheiden. Der Übergang erfolgt bevorzugt an den Bandkanten. Bei hoher Redoxspannung, d.h. tiefem Ferminiveau des Elektrolyten ist der Austausch mit dem Valenzband (als Defektelektronenaustausch formulierbar) bevorzugt, im umgekehrten Fall hingegen der mit dem Leitband. Bei grosser Bandlücke überlappen sich die Terme des Halbleiters mit denen des Elektrolyten aber so wenig, dass praktisch kein Elektronenaustausch möglich ist, wenn man von speziellen Oberflächentermen bzw. Störtermen in der Bandlücke absieht. Die Lage der Bandkanten relativ zum Ferminiveau des Redoxelektrolyten ist bestimmend für die Art des Elektronenüberganges beim Gleichgewicht. Diese Lage und damit der aus Kapazitätsmessungen ermittelbare Leitungscharakter der Halbleiteroberfläche (*n* bzw. *p*) hängt vom Potentialsprung $\Delta\varphi_H$ in der Helmholtzschicht ab. Er hängt daher bei gleichem Halbleiter vor allem von der Natur des Elektrolyten ab, d.h. vom Verhältnis der Konzentrationen der beiden Partner. ($c_{red} > c_{ox}$ begünstigt Leitbandübergänge; $c_{ox} > c_{red}$ begünstigt Valenzbandübergänge.) Weiterhin bestimmt der Unterschied der Ferminiveaus $^\circ E_F$ im isolierten Halbleiter und im Redoxelektrolyt den Mechanismus des Elektronenaustausches beim Gleichgewicht. ($^\circ E_{F,Hl} > {}^\circ E_{F,Redox}$ bewirkt *p*-Leitung (Valenzband); $^\circ E_{F,Hl} < {}^\circ E_{F,Redox}$ bewirkt *n*-Leitung (Leitband). Der wesentliche Anteil des Elektronenüberganges erfolgt im Bereich $4kT$ unterhalb der Valenzbandkante bzw. oberhalb der Leitbandkante mit dem Maximum bei kT ($k \equiv$ Boltzmannkonstante). In Gleichgewichtsnähe erfolgt bei Stromfluss infolge Polarisation der Elektronenübergang ebenfalls bevorzugt dort, wo die Austauschstromdichte am grössten ist. Anodische Polarisation begünstigt grundsätzlich Übergänge in das Valenzband (Defektelektronenaustausch), kathodische solche in das Leitband (Elektronenaustausch). Bei starker Entartung kehren sich die Verhältnisse aber um(!), infolge starker Verschiebung der Bandkanten relativ zu den Termen des Redoxelektrolyten. Vorausgesetzt ist immer eine trotz Stromfluss im Gleichgewicht befindliche Elektronenverteilung im Inneren des Halbleiters. Nur dann ist die Durchtrittsreaktion geschwindigkeitsbestimmend. [H.W.Nür.]

18 – Electrolysis with constant potential: reversible processes at a hanging mercury drop electrode. Irving Shain and Kenneth J. Martin (Dept. of Chem., University of Wisconsin, Madison, Wisc., U.S.A.). *J. Phys. Chem.*, 65 (1961) 254–258.
Results agreed with the classical equations for reactions at tensions where the current was controlled by diffusion alone. Equations for reversible processes taking place at tensions near the equilibrium tension were verified for reactions in which both the reactant and product were soluble in the solution. In cases where the product of the reaction formed an amalgam, the diffusion processes within the hanging mercury drop electrode had to be considered. The suitability of the hanging mercury drop electrode for potentiostatic studies was investigated. [D.S.Ru.]

19 – Electrolysis with constant potential: irreversible reactions at a hanging mercury drop electrode. Irving Shain, Kenneth J. Martin and James W. Ross (Dept. of Chem., University of Wisconsin, Madison, Wisc., U.S.A.). *J. Phys. Chem.*, 65 (1961) 259–261.
The use of the hanging mercury drop electrode for the potentiostatic study of slow electrode reactions was investigated. Assuming a first-order electron transfer reaction and diffusion as the only means of mass transfer, an equation was derived for the current–time curves which takes into account the spherical nature of the electrode. By comparison of experimental current–time curves with a theoretical family of curves, values of the rate constant for the reaction can be obtained from measurements made at times upto 25 seconds after the start of the electrolysis. The reduction of iodate at pH 7.2 was used to test the theory. [D.S.Ru.]

20 – Electrode potentials of the uranium chlorides in fused alkali chloride solutions. S. N. Flengas (Extractive Metallurgy Div., Dept. of Mines and Technical Surveys, Ottawa, Canada). *Can. J. Chem.*, 39 (1961) 773–784.
Using a silver–silver chloride comparison electrode, the electrode tensions of the system U, UCl_3(KCl,NaCl) and the redoxt ensions of the system Pt, UCl_3, UCl_4 (KCl, NaCl) were measured at various concentrations of the uranium chlorides and at temperatures between 650° and 850°. From the results, the electrode tension of the system U, UCl_4 (KCl,NaCl) was calculated. In addition the activity coefficients and partial molal properties of dilute solutions of UCl_3 and UCl_4 in the equimolar mixture of potassium and sodium chlorides were calculated. [D.S.Ru.]

21 – Investigations at thermocouples. V. Electrolytic thermo-elements (in German). R. Haase and P. F. Sauermann (Institut f. physikal. Chemie, Techn. Hochschule, Aachen, Deutschland). *Z. physik. Chem.* (*Frankfurt*), 27 (1961) 42–47.
An electrolytic thermo-element of the following type has been built:

$$\mathrm{Cu}\overset{\varphi}{\underset{T_0}{/}}\mathrm{Pt}/\mathrm{Ag}\underset{T}{/}\mathrm{AgCl}\underset{T}{/}\ \ \mathrm{M^{I}Cl_{aq}}\overset{\varphi_1\ \ \varphi_2}{\underset{T}{/}}\ \ \mathrm{M^{II}Cl_{aq}}\ \ \overset{\varphi_3\,\varphi_4}{\underset{T+\Delta T}{/}}\ \ \mathrm{M^{I}Cl_{aq}}\overset{\varphi_5}{\underset{T}{/}}\mathrm{AgCl}\underset{T}{/}\mathrm{Ag}/\mathrm{Pt}\overset{\varphi+\Delta\varphi}{\underset{T_0}{/}}\mathrm{Cu}$$

$$\varepsilon = \lim_{\Delta T\to 0}\frac{\Delta\varphi}{\Delta T},$$

where $\Delta\varphi$ is the measured tension of the thermocouple.

$$\varepsilon = \varepsilon_{Therm} + \varepsilon_{Diff}$$

$$\text{with } \varepsilon_{Diff} = \lim_{\Delta T\to 0}\frac{\Delta\varphi_{Diff}}{\Delta T} \text{ and } \varepsilon_{Therm} = \lim_{\Delta T\to 0}\frac{\Delta\varphi_{Therm}}{\Delta T}$$

The diffusion may be calculated from the Planck-Henderson equation assuming ideal dilute solutions of 1 : 1-electrolytes of the same concentration and with one common ion. Under these circumstances $\Delta\varphi_{Diff}$ is independent of the structure of the phase boundary. By this method ε_{Therm} may be evaluated from measurements of ε.
Comparision of the above element with two galvanic chains:

$$\mathrm{Cu}\underset{T_0}{/}\mathrm{Pt}\underset{T}{/}\mathrm{Ag}/\mathrm{AgCl}\underset{T}{/}\ \ \mathrm{M^{x}Cl_{aq}}\ \underset{T+\Delta T}{/}\ \mathrm{AgCl}\underset{T+\Delta T}{/}\mathrm{Ag}/\mathrm{Pt}\underset{T_0}{/}\mathrm{Cu}$$

differing only in x = I or II shows that the relation $\varepsilon_{II} - \varepsilon_{I} = \varepsilon_{Therm}$ is obeyed asymptotically.
[H.W.Nür.]

22 – The faradaic admittance of electrochemical processes. II. Experimental test of the theoretical equations. Henry H. Bauer, David L. Smith and Philip J. Elving (Dept. of Chem., University of Michigan, Ann Arbor, Mich., U.S.A.). *J. Am. Chem. Soc.*, 82 (1960) 2094–2098.
The phase angle (φ) between a sinusoidally alternating tension applied to a simple reduction–oxidation system and the resulting faradaic alternating current is a function of the frequency of the electric tension and of the heterogeneous rate constant (k) for the reaction. Two equations have been given in the literature which express this relation; both indicate a proportionality between cot φ and the square root of the frequency, but differ in that one predicts a value of $\varphi > 45°$ and the other a value of $\varphi < 45°$. Using an improved experimental arrangement for the measurement of φ, these two equations have been critically examined for the cadmium–cadmium amalgam system. It was found that either equation may be applied to a narrow frequency range, but that neither yields a constant value for k for wide ranges of frequency or for changes in supporting electrolyte or concentration of electroactive species. It is suggested that the basic postulates used in formulating both equations may be invalid, and that a more rigorous approach might require consideration of the rectifying properties of the electrochemical system. [R.Mur.]

23 – Electrochemical kinetics of the anodic formation of oxide films. Pierre Van Rysselberghe and Hermann A. Johansen (Dept. of Chem. and Chem. Eng., Stanford University, Calif., and Research Laboratories, Westinghouse Electric Corporation, Pittsburgh, Pa., U.S.A.). *J. Electrochem. Soc.*, 106 (1959) 355–358.
An electrochemical theory for the anodic formation of oxide on metals is developed. The electric tension between the metal and the solution at constant current is split up into three components. For the two interphases, metal–oxide and oxide–solution, the cases of linearity of overvoltage with the logarithm of current (large currents)and of proportionality between overvoltage and current (small currents) are discussed. Previously obtained experimental data for three types of titanium and for hafnium and tantalum are reviewed in the light of the proposed theory. Numerical values for the thickness of the interphase, exchange current, electric tension and electric field at zero current are given. [Fe.Jol.]

24 – The anodic oxides of lead. Jeanne Burbank (U.S. Naval Research Laboratory, Washington, D.C., U.S.A.). *J. Electrochem. Soc.*, 106 (1959) 369–376.
The domains of anodic formation of the different lead oxide phases have been represented on a tension–pH diagram. The phases, obtained by potentiostatic methods, have been identified by means of X-ray diffraction patterns. The conditions of formation of α- and β-PbO_2, yellow and

red PbO, and the intermediate oxides, Pb_3O_4 and PbO_x have been determined for acid and alkaline electrolytes. The supposition is made that the intermediate oxides are not directly formed by anodic oxidation, but rather by chemical reaction. The formation of some oxides may be attributable to the preliminary electrochemical oxidation of water. [Fe.Jol.]

25 – Manual of physico-chemical symbols and terminology. J. A. Christiansen (International Union of Pure and Applied Chemistry). *J. Am. Chem. Soc.*, 82 (1960) 5517–5522.
This article is a report of the Physical Chemistry Section (Commission on Physico-Chemical Symbols and Terminology) of the International Union of Pure and Applied Chemistry and contains recommendations for the sign of electromotive force and electrode potential conventions. [R.Mur.]

26 – Faradaic rectification with control of alternating potential variations — application to electrode kinetics for fast processes. Hiroakoi Matsuda and Paul Delahay (Coates Chemical Laboratory, Louisiana State University, Baton Rouge, La.) *J. Am. Chem. Soc.*, 82 (1960) 1547–1550.
If an electrode is in equilibrium with the oxidized and reduced forms, A and B, of a species, and the charge transfer processes $A \rightleftharpoons B$ are rapid, application of an electrical tension varying sinusoidally about the equilibrium tension, E_e, will cause an alternating faradaic current to flow. If the charge transfer process does not occur with equal ease in both directions, the asymmetry of the current–tension curve about E_e will cause the alternating current to be initially asymmetric. There will be a net consumption of one species, a shift in the surface concentrations, and a corresponding shift in the electrode tension. This faradaic rectification will approach zero as the current–tension curve is modified to a symmetrical shape by the concentration changes. The authors have derived equations for the faradaic rectification current and electrode tension shift, which are a function of the electron transfer rate and the frequency of the electrical tension function. These equations should be applicable to the study of fast electrode reactions. The authors have also considered the effect of the structure of the electrical double layer on the rectification current and have derived equations which account for this factor. The equations for the total shift in electrode tension are compared to those obtained by other workers assuming control of the current. [R.Mur.]

27 – Regularities in the activity coefficients of strong electrolytes. M. Moriyama (Electrical Communication Lab., Musashino-shi, Tokyo, Japan). *Z. physik. Chem. (Frankfurt)*, 27 (1961) 34–41.
The dependence of the mean molal activity coefficients $\gamma_\pm$ on concentration is investigated. Three types of electrolytes may be distinguished: (I) $\gamma_\pm$ passes through $\gamma_{\pm\min}$ and then increases again to exceed $\gamma_\pm = 1$ with increasing concentration; (II) $\gamma_\pm$ passes through $\gamma_{\pm\min}$ but does not exceed $\gamma_\pm = 1$; (III) the electrolyte has no $\gamma_{\pm\min}$. In group I the positive ions have small radii and negative ions large radii, so the tendency to form ion pairs is small and the hydration effect large. In group III the cations have large radii and the anions are polyatomic (strong tendency to form ion pairs or even complexes and small hydration effects). Group II has intermediate characteristics. Two regularities are observed: for type I and some members of II. [H.W.Nür.]

28 – Physical-chemical investigation of aqueous ternary electrolyte solutions. III. Investigation of conductivity of system $NaCl–HCl–H_2O$ (in Hungarian). E. Berecz, L. Andras and I. Geiger (Inst. Phys. Chem. Radiology, Eötvös University, Budapest, Hungary). *Magyar Kém. Folyóirat*, 67 (1961) 119–125.
Es wurde die Leitfähigkeit des Systems $NaCl–HCl–H_2O$, bei 25° in gesättigten und ungesättigten Lösungen gemessen. Auf Grund der Messungsergebnisse wurde festgestellt, dass die von NaCl-Zugabe hervorgerufene Leitfähigkeitsänderung von der Anfangskonzentration der $HCl–H_2O$ Lösung abhängt. Der Zusammenhang weist bei einer Anfangskonzentration von 1.5 *M* HCl ein Maximum auf. Es wurde ferner festgestellt, dass sich die Leitfähigkeiten der ternären Lösungen additiv im Verhältnis der Mol-Konzentrationen aus den entsprechenden Leitfähigkeiten der gelösten Komponenten zusammensetzen. In der Kenntnis der entsprechenden Leitfähigkeitswerten, auf Grund der gefundenen empirischen Gleichung, kann die Leitfähigkeit einer beliebigen ternären Lösung mit guter Annäherung einfach berechnet werden. [Ja.Inc.]

29 – The oxygen electrode. I. Isotopic investigation of electrode mechanisms. Myron O. Davies, Milton Clark, Ernest Yeager and Frank Hovorka (Dept. of Chem., Western Reserve University, Cleveland, Ohio, U.S.A.). *J. Electrochem. Soc.*, 106 (1959) 56–61.
The cathodic and anodic properties of the oxygen–peroxide couple have been studied on active carbon electrodes in alkaline solutions, using isotopic techniques involving ^{18}O. The authors have proved that, for the cathodic reaction, all of the peroxide oxygen originates from gaseous oxygen and that the O-O bond is not actually broken during the formation of the peroxide. The anodic oxidation of the HO_2^- ion forms oxygen gas, which contains only peroxide oxygen. Various possible reaction mechanisms are given. [Fe.Jol.]

30 – Contribution to the study of the kinetics of electrode processes (in German). A. Regner and J. Balej (Inst. of Inorg. Chem., Czechoslovak Academy of Sciences, Prague, Czechoslovakia). *Collect. Czechoslov. Chem. Communs.*, 26 (1961) 296–299.
Two modifications of the kinetic equation for simple oxidation–reduction electrode reactions, accompanied by diffusive or activation polarisation, are given. These modifications make it possible to determine the characteristic values of i_0 and α from polarisation curves. [Ot.So.]

31 – The semi-empirical treatment of the regularities in the activity coefficients of strong electrolytic solutions. M. Moriyama (Electrical Communication Lab., Musashino-shi, Tokyo, Japan). *Z. physik. Chem. (Frankfurt)*, 25 (1960) 310–320.
Using Glueckauf's equation for the activity coefficient $\gamma_\pm$ two regularities are examined quantitatively. (1) For each type of electrolyte the plot of $\gamma_\pm$ against the square root of $m_{\min}$ (at the minimum of the $\gamma_\pm - m_{\min}$ curve) gives one curve. (2) Representing the concentration at which $\gamma_\pm$ again equals 1, as m_1 (in mols per 1000 g solvent) the relation $R = m_1/m_{\min} = 5.5 \pm 1$ holds for all types of electrolytes. $R = t^{1/3}\,(1 + 8/3\ t^{-1/3})$, where the variable t depends on the state of the hydrated ion. Also the equation for the curve $\gamma_\pm - \sqrt{m_{\min}}$ is derived and the physical meaning of R is explained. Agreement of the theory with experiment is relatively good. Both regularities have a close interrelation. [H.W.Nür.]

32 – The temperature dependence of dielectric constants (in German). L. Andrussow (Paris, France). *Z. physik. Chem. (Leipzig)*, 215 (1960) 373–379.
Für verschiedene Stoffe wird die Temperaturabhängigkiet der DK (ε)

$$\left(\frac{\varepsilon + \mathrm{d}\varepsilon}{\varepsilon} = \left(\frac{T + \mathrm{d}T}{T}\right)^{n^*}\right)$$

durch Kurven wahrer Exponenten n^* veranschaulicht. Verschiedene Aussagemöglichkeiten der Methode sowie die Reihenentwicklung für $1/n^*$ werden diskutiert und Vergleiche mit anderen Darstellungen der Temperaturabhängigkeit der DK gezogen, sowie mit den mittels der Exponentenmethode für die Temperaturabhängigkeit der Oberflächenspannung gewonnenen Kurven. [H.W.Nür.]

33 – Deposition of ions from aqueous solutions. 2. Deposition of Cs-137- and P-32-phosphate on gold, platinum, and stainless steel. E. Herczynská and I. G. Campbell (Dept. of Radiochemistry, Institute of Nuclear Research, Zerán, Warsaw, Poland). *Z. physik. Chem. (Leipzig)*, 215 (1960) 248–262.
The results of the deposition of the ions named above on the cited metals are in accordance with the assumption that an adsorbed layer of H^+ or OH^- ions in the respective pH ranges favours the approach of anions or cations respectively according to the sign of the electric field in the double layer. [H.W.Nür.]

34 – Deposition of ions from aqueous solutions. I. Deposition of Co-60, I-131-iodide and S-35-sulphate on gold, and platinum foils. E. Herczynska and I. G. Campbell (Dept. of Radiochemistry, Institute of Nuclear Research, Zerán, Warsaw, Poland). *Z. physik. Chem. (Leipzig)*, 213 (1960) 241–261.
The deposition of these ions has been studied as a function of the pH and time of contact of the solution with the metal. The observed deposition behaviour is explained by the covering of the metal surface with H^+ ions at low pH which favours adsorption of anions and repels cations and *vice versa* by adsorbed OH^- ions at high pH. Complications arising from Co-60-radio-colloid formation are discussed. A similar deposition behaviour is observed at non-metallic surfaces, which, in contrast to metals, are not able to form amphoteric hydroxide layers. For metals it is suggested that the deposition mechanism is rather an approach of ions to the electrodes, whether or not attracted by the electric charge of the adsorbed H^+ or OH^- ions in the various pH ranges, than an exchange mechanism. [H.W.Nür.]

35 – Temperature dependence of dielectric constant (in English). W. Dannhauser (University of Buffalo, N.Y., U.S.A.). *Z. physik. Chem. (Leipzig)*, 213 (1960) 225–230.
On the basis of Kirkwood's equation the temperature dependence of the DK of polar liquids such as alkyl halides and water is explained. One may have to deal with several components of the temperature dependence (dipole moment, concentration of dipoles, dependence of the limiting value of DK at high frequencies on T, randomizing effects of thermal agitation on the efficiency of the orientating field proportional to T^{-1}, and variation of the correlation factor g). g takes into account the dipole–dipole orientation by short range intermolecular forces and increases or decreases with T depending on whether the dipoles are orientated in the antiparallel or parallel

position. Plotting the relative DK, deduced by rearranging Kirkwood's equation, against T (between 200° and 350°K) gives over this range straight lines with a slope $g < 1$ for the alkyl halides studied, thus indicating that the antiparallel orientation of dipoles is destroyed at higher temperatures. The results for water ($g > 1$ over the whole temperature range and decreasing with T) are explained on the basis of the hydrogen-bonded structure of water. [H.W.Nür.]

36 – Investigations of galvanic thermo-chains. VI. Evaluation of measurements (in German). R. Haase, K. Hoch and H. Schönert (Institut f. physikal. Chemie, Techn. Hochschule, Aachen, Deutschland). *Z. physik. Chem. (Frankfurt)*, 27 (1961) 421–438.

Aus gemessenen Anfangswerten der Thermokraft galvanischer Thermoketten und den Soret-Koeffizienten der betr. Elektrolytlösungen deren Beträge, ebenso wie die der zur Berechnung gleichfalls erforderlichen molaren Entropien des Elektrodenmaterials und der festen Silberhalogenide, der Überführungsentropie der Elektronen für Cu, der Konzentrations- und Temperaturabhängigkeit des Aktivitätskoeffizienten und der Hittorf'schen Überführungszahlen der Literatur entnommen sind, werden die Überführungsentropien von Cl^-, Br^-, I^-, H^+, NH_4^+, Li^+, Na^+, K^+, Rb^+, Cs^+, Ca^{2+}, Sr^{2+} und Ba^{2+} in wässriger Lösung bei 25° für den Konzentrationsbereich 0.001 bis 0.02 Mol/Kg ermittelt. Um die Auswertungen nicht mit den nur unsicher bekannten Solvatationszahlen zu belasten, werden alle Überführungsgrössen auf die Hittorf'sche statt die Washburn'sche Definition bezogen. Die auf der Basis der Thermodynamik irreversibler Prozesse abgeleiteten allgemein gültigen Ansätze werden eingehend diskutiert. Die ermittelten Standardwerte der Überführungsentropie der Einzelionen sind unabhängig von der Natur des Gegenions. Aus den so ermittelten Werten lassen sich für eine Reihe weiterer Elektrolytkombinationen nun die Soret-Koeffizienten berechnen, was an 25 Beispielen gezeigt wird. [H.W.Nür.]

See also abstracts nos. 135, 175, 192.

2. Apparatus and accessories

37 – A reference electrode for electrochemical studies in fused alkali chlorides at high temperatures. R. Littlewood (Tube Investments Research Laboratories, Hinxton Hall, Saffron Walden, Great Britain). *Electrochim. Acta*, 3 (1961) 270–278.

A comparison electrode based on the silver $\leftrightarrows$ silver chloride reaction has been developed for use in fused halide systems. The electrode has the following useful properties: it is reproducible to better than ±10 mV; it remains constant over long periods in fused alkali chlorides at 700° and is unaffected by freezing and remelting of the electrolyte; it does not contaminate the external melt, since the electrolyte junction is a glass sheath 1 mm thick; it is robust and will even survive solidification of the melt.

Deviation from the Nernst equation has been found and is due to a junction tension across the glass sheath, for which quantitative corrections can be calculated. The transport number of the silver ion through Supremax glass in contact with solutions containing about 0.02–0.5 mole fraction of AgCl in an equimolar NaCl–KCl mixture is negligibly small at 700°. A comparison electrode with an electrolyte concentration of 0.271 mole fraction AgCl in an equimolar NaCl–KCl mixture has a tension of —939 mV with respect to the standard chloride electrode at 700°. [Red.]

38 – Sur le comportement électrique des électrodes de verre. II. Mesure de systèmes aqueux avec des électrodes de verre (en allemand). D. Wegmann, G. M. Lyssy et W. Simon (Laboratoire de chimie organique de l'Ecole polytechnique fédérale, Zürich, Suisse). *Helv. Chim. Acta*, 44 (1961) 25.

Les Auteurs ont étudié 17 électrodes de verre provenant de différents pays (Angleterre, Hollande, Hongrie et Allemagne), en vente dans le commerce. Ils ont déterminé le comportement de celles-ci à divers pH, ils ont estimé l'erreur alcaline en fonction du temps pour des solutions d'hydroxyde de sodium 0.1 *N* et 1.0 *N*, de même que la tension d'asymétrie, la résistance et la stabilité de la tension électrique. [De.Mo.]

39 – An improved electrophoresis apparatus and technique for studying biological cell surfaces. G. I. Gittens and A. M. James (Dept. of Chem., Chelsea College of Science and Technol., London, Great Britain). *Anal. Biochem.*, 1 (1960) 478–485.

An apparatus for microelectrophoresis is described, which overcomes some of the disadvantages

of current techniques. It consists of a rectangular cell constructed according to the theoretical requirements. This is connected to specially designed electrode compartments, and is mounted in a horizontal position under the objective of a microscope. The whole assembly is immersed in a thermostat tank, in which the temperature is controlled within ±0.02°. The electrodes are made of silver foil welded to platinum wire sealed into a glass tube. The electrical circuit and additional apparatus for conductivity measurements are also described.
The results are discussed and a statistical analysis of variables is given. By using a standardised experimental procedure the results are reproducible within ±3%. [Gio.Ser.]

40 – Effect of carboxymethylcellulose on the electrophoresis of serum proteins on paper. R. Holmes and S. W. Wolfe (A. I. DuPont Institute, Wilmington, Del., U.S.A.). *Arch. Biochem. Biophys.*, 87 (1960) 13–18.
Carboxymethylcellulose added to the barbitone buffer used in paper electrophoresis affects the separation of many substances. The effects have been studied on a number of substances including amino acids, proteins, sugars and surface-active agents. In calf serum the addition of carboxymethylcellulose permits the separation of α-lipoprotein from the other fractions, and also the separation of the constituents of the α-lipoprotein fraction from each other. The opportunities for the use of carboxymethylcellulose in electrophoresis are discussed. [Gio.Ser.]

41 – Examination of scanning instruments used in electrophoresis. W. B. Yeoman (Frenchay Hospital, Bristol, Great Britain). *Clin. Chim. Acta*, 5 (1960) 279–282.
A method is described for the evaluation of the performances of optical scanning devices used in paper electrophoresis. It is based on the use of photosensitive paper. [Gio.Ser.]

42 – Simple technique to control the stray field of electrolytic cells. H. P. Schwan and J. Maczuk (Electromedical Div., Moore School of Electrical Engineering, University of Pennsylvania, Philadelphia 4, Pa., U.S.A.). *Rev. Sci. Instr.*, 31 (1960) 59.
This technique is particularly useful in determinations of the dielectric constant of solutions of high conductivity and in biological impedance work. The principle of the theory is based on the plot of the apparent dielectric constant as a function of electrode distance. A logarithmic presentation permits easy determination of the true dielectric constant once the contributions of the stray and polarization terms are assessed from measurements at sufficiently low and high values of electrode distances.
Some experimental results for NaCl solutions are given to demonstrate the applicability of the technique. [G.Mar.]

43 – Determination of moisture in sucrose by means of a high frequency method (in Italian). G. Leonardi, E. Mariani and B. Rumi (Istituto Superiore delle Poste e Telecomunicazioni, Rome, Italy). *Industria saccar. ital.*, 52 (1959) 68–73.
Water content of sucrose can be determined by measuring the change of the dielectric constant of dioxane which has extracted the water from sucrose. A high-frequency electrometric method for the measurement of this change and a suitable apparatus is described. The cell contains the liquid to be measured, two fixed and one variable condenser forming the arms of the capacitance bridge. The measuring cell is made from a double-walled tube containing mercury inside, and surrounded by aluminium foil. The mercury and aluminium foil are the electrodes and the dioxane is contained in the intermediate space. Variations in the dielectric constant of the dioxane unbalance the bridge, and a galvanometer connected to two triodes is used for measuring the changes of capacitance. Details of the apparatus are given and a circuit diagram is shown. [Gio.Ser.]

44 – Arrangement for electrochemical potential–time measurements in the millimicrosecond range. E. Blomgren, D. Inman and J. O'M Bockris (John Harrison Laboratory of Chemistry, University of Pennsylvania, Philadelphia 4, Pa., U.S.A.). *Rev. Sci. Instr.*, 32 (1961) 11–12.
An apparatus is described for electric tension–time measurements at times sufficiently short to allow evolution of double layer capacity and ohmic overpotential, directly from the initial portion of the transient when the determinations have to be performed at times less than 1 millimicrosecond. The capacitance and resistance values thus determined correspond exactly to the conditions during the Faradaic process.
This arrangement has general applicability, and was used to determine i_0 for a silver electrode in a dilute solution of $AgNO_3$ in $NaNO_3$–KNO_3 eutectic at 250° [G.Mar.]

45 – Galvanometer deflection micrometer. O. S. Lutes (Honeywell Research Center, Hopkins, Minnesota, U.S.A.). *Rev. Sci. Instr.*, 31 (1960) 790.
The purpose of this note is to describe a simple photoelectric method which leaves the primary galvanometer circuit unaltered. The method consists of following the position of the primary

galvanometer spot by means of a micrometer coupled mechanically to a photosensitive detector. The sensitivity is such that the position of the primary galvanometer spot can be determined with an accuracy of better than 0.005 mm.
This system can be used when the primary galvanometer serves as a null detector. [G.Mar.]

46 – Stabilizing device for paper electrophoresis (in German). D. Albers. *Ärztl. Lab.*, 5 (1959) 190.
A stabilizing device has been constructed, consisting of a series-connected pentode provided with a large positive grid bias, the current being controlled by the tension in the cathode resistor; 1–3 mA currents are kept constant (±2%), the Joule effect is diminished and higher currents and shorter operation times are attainable. [Ca.Cas.]

47 – Voltamperograph (in Russian). E. D. Kokhman (Institute of Chemical Technology, Kazan, U.S.S.R.). *Zhur. Fiz. Khim.*, 35 (1961) 214–216.
An apparatus is described, with which galvanostatic and potentiostatic studies of anodic and cathodic processes can be made, as well as chronopotentiometric investigations connected with the applied cell voltages and changes in the current-free electrode tension. [Ot.So.]

48 – Apparatus for continuous electrophoresis (in Russian). V. P. Shedov and A. V. Stepanov. *Zhur. Fiz. Khim.*, 35 (1961) 217–219.
An arrangement for continuous electrophoresis on a continuous column is described. The arrangement can be used both for the separation of mixtures and the determination of ion mobilities. The original paper includes detailed drawings and wiring diagrams. [Ot.So.]

49 – Deionized water by electrodialysis. J. A. Schufle (New Mexico Institute of Mining and Technology, Socorro, New Mexico, U.S.A.). *J. Chem. Ed.*, 38 (1961) 17–19.
Water purified by electrodialysis is suitable for many applications in which distilled water is conventionally used, and may be produced at less than 1% of the cost.
A cell consisting of thirty compartments separated by Permutit ion exchange membranes 3142 and 3148 and capable of producing 2 gal/h is described. [D.S.Ru.]

50 – Student experiment with filter paper electrophoresis. James E. Garvin (Dept. of Biochem., Northwestern University Medical School, Chicago, Ill., U.S.A.). *J. Chem. Ed.*, 38 (1961) 36–37.
The construction and operation of an inexpensive electrophoresis apparatus is described. Satisfactory separations of various amino acids and several haemoglobins were obtained. [D.S.Ru.]

51 – High frequency titrimeter and its use (in Hungarian). E. Pungor (Dept. of Inorg. and Anal. Chem., L. Eötvös Univ., Budapest, Hungary). *Chem. Zvesti*, 13 (1959) 823–826.
An apparatus is described for titrations at 130 Mc/sec. The apparatus can be used in neutralisation titration and in the study of the stability of solutions in closed glass vessels. [Gio.Ser.]

52 – Use of four-electrode conductometry for the automatic determination of carbon dioxide and ammonia in concentrated scrubbing water of coke oven gas. E. Barendrecht and N. G. L. M. Janssen (Central Lab., Limburg State Mines, Geleen, The Netherlands). *Anal. Chem.*, 33 (1961) 199–203.
The construction of an apparatus for the automatic determination of ammonia and carbon dioxide in aqueous solutions contaminated with oil and tar and similar substances is described. Two electrodes carry a 50–60 pulse/sec alternating current through the solution to be analyzed and the tension is measured with two other electrodes. A cell of special construction is used. The complete wiring diagram and construction details of the apparatus and cell are given. The conductometry of the system ammonia–carbon dioxide–water is studied. The standard deviation in ammonia determination is 2.8% and of carbon dioxide 1.3%. [Kl.Gr.]

53 – A simple micro volumetric combustion polarographic cell. R. M. Parkhurst (Stanford Research Institute, Menlo Park, Calif., U.S.A.). *Anal. Chem.*, 33 (1961) 320.
The polarographic determination of traces in combination with combustion of the material can be simplified by carrying out the weighing, combustion, dilution and polarography in one apparatus. The construction of such a cell of borosilicate or Vycor glass is described. A drawing of the cell and a description of the analytical procedure is given. [Kl.Gr.]

54 – New apparatus for electrolytic isolation of carbides and non-metallic inclusions from steel. A. Fiala, J. Macek and V. Štádler (Z.V.I.L., Llzeň, Czechoslovakia). *Hutnické Listy*, 15 (1960) 55–56.
An apparatus is described which has a very high efficiency in dissolving samples, low consumption of electrolyte and which dissolves the anode from all sides. The possibility of adjusting the current

to the same density for each sample is included and various electrolytes can be used. The electrolyte can be cooled and the whole process may be carried out in an inert atmosphere. Part of the apparatus is made of polystyrene instead of glass, this being very advantageous. [Gio.Ser.]

55 – Preliminary studies on quantitative zone electrophoresis in starch gel. J. H. Pert, R. E. Engle, K. R. Woods and M. H. Sleisinger (New York Hosp., Cornell Med. Center, New York, U.S.A.). *J. Lab. Clin. Med.*, 54 (1959) 572–584.
In this procedure the buffer and the starch for making the gel are accurately standardised. The staining is carried out under controlled conditions, and a reflectance densitometer is used. The resolution and reproducibility are greatly improved. The results obtained with normal and pathological human sera are shown and discussed in comparison with the results obtained in similar cases by other electrophoretic methods and by ultracentrifugation. [Gio.Ser.]

56 – Improved protein resolution of concentrated tissue extract in zonal column electrophoresis. S. Sorof, E. M. Young, M. M. Spence and P. L. Fetterman (Inst. Cancer Research, Philadelphia, Penn., U.S.A.). *Biochim. Biophys. Acta*, 38 (1960) 559–561.
Columns of ethanolised cellulose are used according to the method of Porath, for the electrophoretic separation of proteins. Closing the columns with membranes of regenerated cellulose improves the resolution and allows a more accurate control of the separation conditions. [Gio.Ser.]

57 – New clinical method for measuring dissolved and bound oxygen in blood electrochemically. (in German). K. Damaschke and E. Saling (Federal Establishment for Materials Testing, Berlin-Dahlem, Germany). *Klin. Wochschr.*, 37 (1959) 826–828.
An apparatus is described for measuring oxygen by measuring the current generated during its reduction to OH^-. The measuring cathode is gold amalgam and the comparison anode is zinc immersed in a tube containing saturated KCl solution. The anode compartment is connected to the measuring solution in which the cathode is immersed, through a diaphragm. The current is measured with a very sensitive galvanometer. [Gio.Ser.]

58 – Simple apparatus for the coulometric titration and determination of zinc by the generation of potassium ferricyanide. P. K. Agasyan. *Vestnik Moskov. Univ.*, (1959) 156–162.
Potentiometric and amperometric methods are very suitable for end-point detection in the determination of Zn^{2+}. By using a very simple apparatus concentrations of 180–3000 µg of Zn^{2+} in 50 ml of solution have been determined with great accuracy. These quantities are lower than those previously reported in the literature. [Gio.Ser.]

59 – Preparation and properties of acrylamide gel for use in electrophoresis. S. Raymond and Yi-Ju Wang (Pepper Laboratory, University of Pennsylvania, Philadelphia, Penn., U.S.A.). *Anal. Biochem.*, 1 (1960) 391–396.
Acrylamide monomer can be polymerised in suspension in a buffer of any desired pH. A gel is obtained under these conditions, which can be successfully used in electrophoresis. In practice 5 g of the monomer (Cyanogum 41, American Cyanamide Co.) are suspended in 100 ml of the buffer. To this suspension 1 ml of a freshly prepared solution of dimethyl aminopropionitrile (10%) and 1 ml of a 10% solution of ammonium persulfate are added, and the solution is kept in a suitable frame for three hours, until it gels. The gel so obtained is used for carrying out the electrophoresis. The apparatus used is described. The gel must be cooled on both sides because of its high water content. With the conditions described 300 V can be applied with a current of 180 mA. Optimal separations of proteins are obtained. On further lowering the gel concentration, the mobilities are increased. [Gio.Ser.]

60 – Use of electrodes screened by some polymers in the potentiometric indication of the end-point. K. Komers (Dept. of Chem. Anal., Inst. Chem. Technol., Pardubice, Czechoslovakia). *Sbornik věd. prací, Vysoká škola chem.-technol., Pardubice,* (1959) 113–119.
The electrodes were prepared by immersion in solutions of polystyrene or poly(methyl methacrylate) in acetone, or polyvinyl chloride in *cyclo*hexanone, or chloroprene in $CHCl_3$. The solutions used were 0.5–5%. After drying for 20 min in air, the electrodes were used in various redox and argentimetric titrations. The results obtained were very good. [Gio.Ser.]

61 – How to measure small conductivities with contactless measuring cells at low frequencies. (in German). F. Oehme (Institut Entwicklg. chem. phys. Analysenmeth., Weilheim/Obb., Deutschland). *Mitt. Inst. Entw. chem.-phys. Analysenmeth.*, 4 (1960) 81–89.
Die Messung kleiner Leitfähigkeiten unter Verwendung von Kohlrausch-Zellen setzt bei höheren

Genauigkeitsansprüchen zunächst eine Korrektur des gemessenen Zellenwiderstandes im Hinblick auf die Parallelschaltung eines kapazitiven Gliedes und die dadurch bedingte Messung eines verfälschten Scheinwiderstandes voraus. Diese Korrektur wird mit Beispielen belegt. Weiter wird gezeigt, dass bei Verwendung kontaktloser Messzellen, wie sie in der Hochfrequenz-Titration üblich sind, bei Anwendung niedriger Messfrequenzen auch noch Leitfähigkeiten bis herab zu etwa 10^{-10} Ohm^{-1} cm^{-1} gemessen werden können. Für den Fall des NF-Dekameters werden Kennkurven der Blindkomponenten-Methode im Bereich von 200 Hz bis 100 kHz dargestellt und die theoretischen Deutungen gegeben. [Fr.Oe.]

62 – Conductivity measurements — the influence of erratic fields (in German). H. Karner (Institut Entwicklg. chem. physik. Analysenmeth., Weilheim/Obb., Deutschland). *Mitt. Inst. Entw. chem.-phys. Analysenmeth.*, 4 (1960) 73–80.
Es wird gezeigt, dass bei Widerstandsmessungen mit den üblichen Kohlrausch-Zellen der Einstreuung von Fremdfeldern als Störquelle bei Präzisionsmessungen Beachtung zu schenken ist. Das trifft besonders dann zu, wenn die Apparatur mit Netzfrequenz (50 Hz) arbeitet und es sich um Fremdfelder derselben Frequenz handelt. Der Einbau von 50 Hz-Sperren verbietet sich in diesem Falle. Die Messergebnisse müssen folglich rechnerisch korrigiert werden. Für einen bestimmten Modellfall wird die Fehlerfunktion angegeben und ein Auswertungs-Diagramm dargestellt. [Fr.Oe.]

63 – Tri(hydroxymethyl)methylamine as an electrophoresis buffer. R. D. Rapp and M. M. Memminger (The Reading Hospital, West Reading, Pa., U.S.A.). *Am. J. Clin. Pathol.*, 31 (1959) 400–403.
The separation of serum proteins is improved by the use of Tris (tri(hydroxymethyl)methylamine) buffer. The shape of the spots obtained was not regular so that planimetry was difficult. By using a mixture of Tris and barbitone buffer of total ionic strength 0.07 a very good separation was obtained in half the time required by the usual methods. [Gio.Ser.]

64 – Dialysis studies. III. Modification of pore size and shape in cellophane membranes. L. C. Craig and W. Konigsberg (Rockefeller Inst. Labs., New York, U.S.A.). *J. Phys. Chem.*, 65 (1961) 166–172.
An investigation has been made of various ways of modifying the porosities of cellophane dialysis membranes. Mechanical stretching, acetylation and zinc chloride treatment have been found effective. Optimum porosities for studying solutes with molecular weights varying from those of dipeptides to 100,000 (proteins), can be determined at will. [D.S.Ru.]

65 – Microwave absorption and molecular structure in liquids. XXXIV. An interferometric method for measurement of dielectric constant and loss at 4.3 mm wave length. W. E. Vaughan, K. Bergmann and C. P. Smyth (Frick Chemical Laboratory, Princeton University, Princeton, N.J., U.S.A.). *J. Phys. Chem.*, 65 (1961) 94–97.
The theory and apparatus for an interferometric method for the measurement of the dielectric constant and loss of liquids at 4.3 mm wave length are described. The probable error of the dielectric constant measurement is 1%, except for extremely low loss materials, in which case the error increases as the loss decreases. The probable error of the loss measurements is 2%, increasing for both extremely high loss and extremely low loss. [D.S.Ru.]

66 – A constant cathode potential electrodeposition apparatus. N. J. Wadsworth (Metallurgy and Physics Dept., Royal Aircraft Establishment, Farnborough, Hants., Great Britain). *Analyst*, 85 (1960) 673–680.
In a three-electrode cell the cathode comparison electrode tension is balanced against the required electrical tension derived from a potentiometer. The error voltage is fed to a high-gain d.c. transistor amplifier, the output of which provides the cell current which varies so as to maintain the error voltage to within ±5 mV. Current from 0–8 A at cell working tensions of 0–6 V are suitable. The control tension can be set at any value from —3 to +3 V. A complete circuit diagram is given. [P.O.Ka.]

67 – Electrophoretic apparatus with automatic registration of the extinction curve (in Russian). B. N. Zeliger (Leningrad Pediatric Institute, Leningrad, U.S.S.R.). *Lab. Delo*, 6 (1960) 55–59.
An apparatus is described combining an electrophoresis apparatus, for carrying out paper electrophoresis, with a densitometer and an automatic recorder for the registration of the extinction of the electropherogram and the determination of the separated bands. [Gio.Ser.

68 – An apparatus for paper ionophoresis. S. Lovett (Microbiological Research Establishment. Porton, Nr. Salisbury, Wilts., Gt. Britain). *Chem. & Ind.*, (1960) 709–710.
The construction of a tank suitable for the processing of several papers at one time is given in detail. It consists chiefly of perspex with electrodes of nickel and aluminum. [D.S.Ru.]

69 – Use of a compensator of polarographic currents for the preparation of products of the electrode processes on the mercury drop electrode (in German). J. Peizker (Polarographic Inst., Czechoslovak Academy of Sciences, Prague, Czechoslovakia). *Collect. Czech. Chem. Communs.*, 26 (1961) 230–236.
A photocompensator of polarographic currents is used as a potentiostat to prepare in a short time sufficient amounts of the products of the electrode reaction to identify them and sometimes even to determine them. [Ot.So.]

70 – Electrical impedance at the surface of $Pd/H/H_2$-electrodes. J. C. Barton, F. A. Lewis, D. S. McIlhagger and R. K. Quigg (Dept. of Chem., Queen's University, Belfast, N.Ireland). *Naturwissenschaften*, 48 (1961) 216–217.
The impedance of a pair of palladized Pd-electrodes (wires, 3 cm long, 0.0122 and 0.0274 cm diameter, hydrogen saturated, 1 N HCl, 25°) was studied with an a.c. bridge. With a balancing circuit I of resistance R_1 and capacity C_1 parallel to it, the impedance showed a marked frequency dependence. Putting another resistance R_2 in series with circuit I, where R_2 equals the value of R_1 for high frequencies and the sum $R_1 + R_2$ is approximately equal to the low frequency value of R_1 in circuit I, no frequency dependence of balance was observed in the range 20 to 5000 Hz. This method is of value for the investigation of the formation of films on Pd thus inhibiting adsorption of hydrogen. [H.W.Nür.]

71 – Circuits for impedance measurements for the investigation of electrode reactions at high frequencies (in German). W. Lorenz (Institut f. physik. Chemie, Universität Leipzig, Deutschland). *Z. physik. Chem. (Frankfurt)*, 26 (1960) 424–434.
Two T-bridges for impedance measurements at polarized electrodes are described. Results concerning the mechanism and velocity of molecule adsorption at mercury electrodes and the velocity of association reactions in the adsorption layer are also reported. The influence of association becomes higher the larger the size of the adsorbed molecules. [H.W.Nür.]

72 – The faradaic admittance of electrochemical processes. I. Apparatus suitable for phase angle measurement. Henry H. Bauer and Philip J. Elving (Dept. of Chem., University of Michigan, Ann Arbor, Michigan, U.S.A.). *J. Am. Chem. Soc.*, 82 (1960) 2091–2094.
In the study of the effects of the application of a small sinusoidal alternating tension (V) to an electrochemical system (as in alternating current polarography), the measurement of the faradaic alternating current (Ir) is complicated by the necessity of correcting for the electrical double layer capacitance (which involves consideration of the phase angle between V and the alternating current) and the series resistance of the cell. An improved experimental arrangement is described which permits measurement of the series resistance, the double layer capacitance, and the phase angle between V and the total alternating current. The phase angle measurement is accomplished by oscilloscopic comparison with the phase angle of a variable resistor and capacitor in parallel and in the experimental circuit. Theoretical equations for the experiment are given for the calculation of Ir, the alternating tension (Vr) actually operative at the electrode, and the phase angle between Ir and Vr. The procedures for all the necessary experimental measurements are given in outline form. [R.Mur.]

73 – Measuring equipment for polarization studies in distilled water. J. E. Draley, W. E. Ruther, F. E. DeBoer, and C. A. Youngdahl (Argonne National Laboratory, Lemont, Ill., U.S.A.). *J. Electrochem. Soc.*, 106 (1959) 490–494.
An apparatus, suitable for polarization measurements in low conductivity solutions, is described. The usual measuring methods are discussed and found inapplicable. The details of the experimental cell are given and an application of the equipment to the study of the polarization of aluminium in boiling water is demonstrated. [Fe.Jol.]

74 – Investigation of N-methylacetamide as a non-aqueous polarographic solvent. D. E. Sellers and G. W. Leonard, Jr. (Dept. of Chem., Kansas State University, Manhattan, Kan., U.S.A.). *Anal. Chem.*, 33 (1961) 334.
N-methylacetamide is proved to be a suitable solvent for polarographic reduction in non-aqueous media. Tetraethylammonium bromide is used as the supporting electrolyte. The tension of the

mercury pool electrode is reproducible within ± 0.003 V. The influence of atmospheric moisture on the half wave value and the diffusion current constant, and the linearity of the diffusion current *vs.* concentration plot for inorganic and organic compounds are studied. The interference of oxygen, reversibility of the electrode process, formation of maxima and utilisation of maximum suppressors are also investigated. The following compounds are studied CdI_2, PbI_2, O_2, *p*-nitroaniline, *p*-nitroacetanilide, 4,4′-bis-acetamino-azoxybenzene, azobenzene, benzil. [Kl.Gr.]

75 – Techniques for the application of polarography to mitochondrial respiration. B. Hagihara (Institute for Enzyme Research, University of Wisconsin, Madison, Wis., U.S.A.). *Biochim. Biophys. Acta*, 46 (1961) 134–142.
An apparatus for the measurement of oxygen consumption by biological materials is described. A rotating platinum electrode is used, and this is coated by immersion in a collodion solution to improve the sensitivity and reproducibility of the results. A specially constructed cell is described, which allows the carrying out of the measurements and the addition of reagents without the entrance of oxygen. The sources of error in the measurements of the respiration of mitochondria are discussed together with the performances of the electrode. The errors may be eliminated by the use of the electrode and the cell described. [Gio.Ser.]

76 – A simple apparatus for immunoelectrophoresis (in German). G. Zimmermann and K. Krüger (Forschungs-Institut für Impstoffe, Dessau, Deutschland). *Pharmazie*, 14 (1959) 222–223.
A very simple apparatus for horizontal immunoelectrophoresis on agar films is fully described: there are two compartments for the anodic and cathodic buffer solutions respectively and the graphite electrodes are separated from the solution by a plaster diaphragm. The gel film is made from purified agar containing a veronal buffer at pH 8.6. The agar is purified by dialysis *vs.* water for 3 days; the hot 4% solution is filtered (through G4 sintered glass), diluted with the same volume of buffer solution and placed on the glass supporting plate (2 ml for a 1 mm thick film). A 0.001 — 0.003 ml sample is placed in two positions 8 mm apart. Electrophoresis is carried out by applying 120 V (5 mA, 7 V/cm) for 45 min. Thereafter a 1 mm wide cut is made between the two pherograms which is then treated with 0.05 — 0.1 ml antiserum. The results obtained for an ox normal serum and for an ox crude albumine fraction are reported. [G.deAn.]

See also abstracts nos. 117, 140, 224, 246, 282, 340.

3. Polarography

77 - Direct polarographic determination of tin in the presence of lead, thallium, arsenic and antimony. Determination of small concentrations of tin in lead (in Polish). M. Cyrankowska (Anal. Lab., Central Laboratory of Accumulators and Cells, Poznań, Poland). *Chemia anal.*, 5 (1960) 851–861.
The polarographic behaviour of tin(IV) in acid EDTA solutions has been studied. In high concentrations of chloride one or two waves were observed depending on the acidity. The height of the first wave was independent of the pH in the range 1–3, and had a diffuse character. The presence of organic complexing agents such as tartrate, citrate and acetate did not influence the wave height. The concentration of chloride must be carefully controlled. Analytical determination was possible when an acid (pH 1–2) supporting electrolyte was used, containing 0.01 *M* EDTA, and 2.7 *M* NaCl. Under these conditions the waves of Pb, Tl, Cd, Bi and Cu were sufficiently separated, and As, Sb, Ni, Co, Zn, Mn, Al and Cr were not reduced at all. At pH 2.0 the reduction wave of tin had $E_{1/2} = -1.03$ V (*vs.* S.C.E.) On this basis a procedure for the determination of 0.0005% Sn in lead was developed. The majority of lead was removed as $PbSO_4$. When silver was present it was necessary to remove it as AgCl. The presence of As and Sb was masked by oxidation with potassium permanganate. This method can be therefore applied to the analysis of Pb/Sb alloys. The relative error was 2–6%. [Ad.Hu.]

78 – Catalytic determination of microgram amounts of iodide using amperometry (in Polish). K. Czarnecki (Dept. of Inorg. Chem., University of Łódź, Poland). *Chemia anal.*, 5 (1960) 875–880.
Microamounts of iodide catalyze the reaction between arsenite and ceric ions. The reaction rate is a function of the iodide concentration and the half-life time is inversely proportional to the io-

dide concentration. The changes of ceric ion concentration were measured by means of amperometry without external voltage. As the indicator electrode platinum wire was used; a saturated calomel electrode was used as the comparison electrode. Iodide was determined in 0.12 to 0.76 μg of solutions in which its concentration was of the order of 10^{-9} g/ml. The precision was about 2.5%. This method was used for lead iodide solubility determination and results differing by 2.5% from the data given in the literature were obtained. [Ad.Hu.]

79 – Amperometric determination of metals with thioacetamide. I. Determination of silver (in Polish). M. Pryszczewska (Dept. of Gen. Chem., Politechnika, Szczecin, Poland). *Chemia anal.*, 5 (1960) 931–934.
Silver solutions of concentrations approx. 10^{-3}–10^{-4} M were titrated with thioacetamide. The end-point was detected amperometrically with a dropping mercury electrode as an indicator electrode at —0.4 V *vs.* S.C.E. During titration the solutions were deaerated with hydrogen. A linear calibration curve was obtained. The method was simple and reproducible. When 1.7–10.2 mg Ag was titrated errors were in general less than 0.07 mg. [Ad.Hu.]

80 – Application of phosphate buffers in polarographic investigation of ascorbic acid (in Polish). Z. Bożyk and S. Krauze (Dept. of Food Products, Faculty of Pharmacy, Academy of Medicine, Warsaw, Poland). *Chemia anal.*, 5 (1960) 993–1003.
It has been stated that phosphate does not form any adsorption film on the dropping mercury electrode which interferes in the determination of ascorbic acid using its anodic wave. In these investigations no interference in the electrode processes was observed. When metaphosphoric acid was added to phosphate buffers no maxima of ascorbic acid were observed. In concentrations of 0.6% metaphosphoric acid was found to be a good surface-active substance. No disadvantages noted for other surface-active agents were observed in this case. [Ad.Hu.]

81 – Polarographic determination of the solubility product of thallium(I) sulfide (in English). P. Kivalo and Rakel Kurkela (Finland Institute of Technology, Helsinki, Finland). *Suomen Kemistilehti*, 32 (1959) B 39–40.
The thermodynamic solubility product of thallium(I) sulfide has been determined polarographically. The value at 25° is $pK_{s0} = 20.0$. [Sta.Bred.]

82 – Etude comparative concernant la réduction de l'acide benzoïque et des acides monoaminobenzoïques à goutte de mercure (en allemand). A. M. Shams El Dim et G. Trümpler (Laboratoire de chimie physique et d'électrochimie de l'E.P.F., Zürich, Suisse). *Helv. Chim. Acta*, 44 (1961) 48.
L'acide benzoïque et les trois acides monoaminobenzoïques en solution sulfurique diluée, avec et sans addition d'éthanol, sont réduites électrolytiquement sur une cathode au mercure. La variation du rendement de courant global en fonction du temps révèle un caractère similaire pour les quatre acides. A côté des alcools, il se forme des produits de réduction plus poussée. Des observations de confrères et des Auteurs plaident en faveur du fait qu'il s'agit d'acides hydrogénés dans le noyau. La formation d'aldéhyde ne put être décelée dans aucun acide.
La tension cathodique pour les quatre acides est à peu près semblable pour une même intensité de courant, ce qui montre que l'on doit considérer comme un phénomène primaire la charge donnant des ions hydrogènes. Avec des acides aminobenzoïques, les rendements de courant sont plus grands que dans le cas sans éthanol.
La comparaison des rendements en tant que mesure de l'activité de la réduction pour des expériences sans addition d'éthanol et pour des intensités de courant pas trop grandes, montre la succession attendue de la réductibilité des trois acides monoaminobenzoïques à savoir $m > o > p$. [DeMo.]

83 – Review of methods for determination of lead in cast iron. R. C. Rooney (B.C.I.R.A., Research Dept., Alvechurch, Birmingham, Great Britain). *Brit. Cast Iron Research Assoc. J.*, 8 (1960) 360–376.
The methods for the determination of lead in concentrations ranging from 0.0001 to 0.01% are reviewed and discussed. Gravimetric methods are not satisfactory. Direct polarographic methods undergo interference by Sn, Tl, As and Mo, and may be used only when the concentration of these elements is small in comparison to that of Pb. Square-wave polarographic methods give good results if interference from Sn is eliminated, and that from Tl is calculated. The only methods substantially free from interference are the dithizone colorimetric method, and the polarographic methods based on extraction. [Gio.Ser.]

84 – The polarographic determination of papaverine. L. Faith (State Institute for Control of Drugs, Bratislava, Czechoslovakia). *Farmácia*, 29 (1960) 79–81.
A method for the determination of papaverine by conversion to the nitro derivative, and polaro-

graphy of the latter is described. The nitration is carried out by adding 1 ml of HNO_3 (65%) to a sample, heating for 30 min at 60°–80° on a water bath, cooling and adding 10 ml of 20% KOH, and 0.1 ml of 0.5% gelatin. After 15 min the oxygen is removed and the polarogram is recorded, starting from —0.4 V. The nitro compound shows a double wave, the first portion of which can be used for the quantitative determination of papaverine. This method is suitable for determination of tablets, and using a calibration curve the error is not greater than ±3%. [Gio.Ser.]

85 – Polarography of aromatic hydrocarbons and related substances (in English). G. J. Hoijtink (Chemical Lab., Free University, Amsterdam, The Netherlands). *Ricerca sci.* (Suppl. No. 5, Contributi di Polarografia), 30 (1960) 217–228.
After a wide survey of the literature on polarography of conjugated hydrocarbons, experimental evidence is given for their reduction mechanism in the absence of proton donors in terms of (i) addition of an electron to the molecule, and (ii), at more negative tensions, addition of an electron to the mononegative ion. An electrode reaction is assumed which is reversible when the maximum faradaic current in a.c. polarography increases in direct proportion to the square root of the a.c. frequency. Theoretical conclusions are drawn on the influence of the electric field in the electrode double layer and on selective and non-selective reductions. [Fr.Pan.]

86 – A general equation for the effect of substituents on half-wave potential (in English). P. Zuman (Polarographic Institute, Prague, Czechoslovakia). *Ricerca sci.* (Suppl. No. 5, Contributi di Polarografia), 30 (1960) 229–259.
The shift of $E_{1/2}$ in a series of organic compounds with one characteristic polarographically active group but having different substituents, are explained in terms of polar resonance and steric effects. Examples of a quantitative treatment based on the linear free energy relationship are given which may be used when only polar effects play an important role. Applications are given of the special forms of the general equation for the shift of $E_{1/2}$ for benzenoid, heterocyclic, aliphatic and quinoid compounds and experimental conditions are discussed. [Fr.Pan.]

87 – The influence of the chemical structure on polarographic parameters in heterocyclic chemistry (in French). J. Tirouflet and M. Person (Lab. chimie gén., Faculté de Sciences, Dijon, France). *Ricerca sci.* (Suppl. No. 5, Contributi di Polarografia), 30 (1960) 269–276.
The following heterocyclic compounds, with a reducible side chain, were investigated polarographically: thiophene, pyridine, pyrrole, thiazole, imidazole and ferrocene. The influence of the ring on the shape of the waves was interpreted either by the fact that the heterocyclic ring was acidobasic or by the electronic influence of the heteroatom upon the functional group. [Fr.Pan.]

88 – Constitution and temperature dependence of electronic spectra and polarograms of (β-hydroxyalkylamino)-*p*-benzoquinones (in German). H. Berg, K. H. König, D. Tresselt and H. Wagner (Institut für Mikrobiologie, Jena, Germany). *Contributi di Polarografia, suppl. Ricerca sci.*, 5 (1960) 277–295.
Electronic spectra and polarographic characteristics are given for more than 30 quinone derivatives and their physicochemical properties are discussed. These compounds, when in the dissolved state, are in an equilibrium such that two steps are involved in carrying out the thermochromy and the polarographic reduction. Polarographic and spectroscopic measurements allow conclusions to be drawn on the constitution of both forms in equilibrium. [Fr.Pan.]

89 – A simple polarographic method for determining lead in must and wine (in German). E. Gilbert and H. Grohmann (Chem. Invest. Bureau, Spires, Germany). *Deut. Lebensm. Rundschau*, 55 (1959) 300–303.
The method is as follows: 3 ml 10% HNO_3 (free from lead) are added to the carbon-free ash obtained from a 50 ml sample; this is brought to dryness in a water-bath heated at 500°. 2 ml of 2 *N* HCl are added to the residue, the solution transferred to the polarographic cell, and, after washing with twice-distilled water (2 × 1 ml), made up to 5 ml with the same water. After addition of 1 ml of 1 *N* LiCl as supporting electrolyte and 1 ml of 0.1% gelatine solution as maximum suppressor, any interfering Fe^{3+}, Cu^{2+} and Zn^{2+} are eliminated with 1 ml of 0.5% potassium ferrocyanide; nitrogen (or hydrogen) is then bubbled through the cell and the polarographic determination is carried out by means of a recording instrument (sensitivity 1/20 at 1 drop/2.6 sec).
The wave-height is then measured by a graphic extrapolation and the Pb content of the sample calculated by means of a calibration curve. The absence of Pb in the reagents must be checked polarographically. [Ca.Cas.]

90 – Polarographic determination of tartaric acid (in German). G. Brockelt and R. Pohloudek-Fabini (The University, Greifswald, Germany). *Pharmazie*, 14 (1959) 377–380.

The method is based on the transformation of tartaric acid into a polarographically active product (glyoxal), which is then determined.
A 5 ml sample (approx. 0.1 *M*), to which 0.5 ml of (0.1 *M*) uranyl acetate have been added, is irradiated with a 800 W quartz-lamp for 30 min, brought to pH within the range 6.3–6.8 with 0.4 *M* Na_2HPO_4 (1 ml), boiled, made up to 6.5 ml and filtered on G_3 sintered glass. 0.1 ml of 40% NaOH are added to 5 ml of the filtrate deaerated with nitrogen and after a 10 sec additional deaeration, polarography is started from —1 V (t = 3.17 sec, m = 2.78 mg/sec in air under 44 cm Hg).
The measurements are carried out with the aid of calibration curves, care being taken that the times after the NaOH addition are the same, owing to the variations of the wave-height with time. [Ca.Cas.]

91 – Water determination in serum. P. Paaby (County Hospital and Municipal Hospital, Aalborg, Denmark). *Scand. J. Clin. & Lab. Invest.*, 11 (1959) 117–121.
Two methods for the determination of water content in serum are compared: the Karl Fischer method is less exact, requires more expensive and sensitive apparatus and reagents, gives constantly higher values (0.2%), but is quicker; the gravimetric method (dry a 0.5 ml sample at 70° and 23 mm Hg for 16 h) gives more reproducible values and is more simply executed. [Ca.Cas.]

92 – Microdetermination of potassium in serum. N. P. Penceff (The University, Sofia, Bulgaria). *Rev. chim. (Bucharest)*, 10 (1959) 349–351.
In the solution to be titrated, K is precipitated by means of a solution of sodium cobaltinitrite (45 g of the salt, 19 g of sodium acetate, 18 g of acetic acid in 120 ml of H_2O) drop by drop and then diluted with 1 vol. of alcohol; after 1 h or more, the precipitate is filtered by means of a filter-stick according to Pregl, washed with 2–3 ml buffer (1% acetic acid–1% sodium acetate = 1 : 1) and then with 70% ethanol (5–7 ml); after dissolution in dilute HCl and evaporation to dryness, the residue is taken up in 0.1 *N* HNO_3, treated with excess NH_3–NH_4NO_3 (0.1 *N*) solution and Na_2SO_3 and polarographed after addition of drops of methyl-red as maximum suppressor.
From the amount of Co obtained in this way, the K content is calculated on the basis of the formula $K_{1.84}Na_{1.16}[Co(NO_2)_6]$ for the precipitate obtained under the above conditions.
A photocolorimetric procedure is also described, based on the precipitation as $K_3[Bi(S_2O_3)_3]$, and successive determination of the Bi as $[BiI_4]^-$. [Ca.Cas.]

93 – Determination of ultramicro-concentrations of substances in solution by the method of amalgam polarography on the stationary drop electrode (in Russian). A. G. Stromberg and E. A. Stromberg. *Zavodskaya Lab.*, 27 (1961) 3.
A review dealing with the determination of concentrations in the range 10^{-7}–10^{-9} *M*. The following topics are discussed: various types of stationary mercury drop electrodes (with diagrams); the conditions of preliminary electrolysis and their influence on the depth of the anodic incision; influence of the conditions of the oscillographic measurement on the depth of the anodic incision; and the simultaneous determination of a number of elements in the solution. A special chapter is devoted to the purification and storage of reagents. It is stated that the sensitivity of the method described is 100–1000 times better than conventional polarography. Minimum concentrations that can be determined are given for a number of elements. Among ways of further increasing the sensitivity are mentioned the following: more intensive agitation during electrolysis; increase of the rate of tension change; the use of a differential method; and the use of purer reagents. [Ot.So.]

94 – Polarographic investigation of the iodomethyltrialkylsilanes. Unusual polarographic maximum on the iodomethylphenyldimethylsilane wave (in Russian). S. G. Nairanovskii, V. A. Ponomarenko, N. V. Barashkova and A. D. Snegova (Institute of Organic Chemistry, Academy of Sciences, Moscow, U.S.S.R.). *Doklady Akad. Nauk S.S.S.R.*, 134 (1960) 387–390.
The authors have investigated the polarographic behaviour of organic molecules containing silicon. The following were investigated: iodomethyltrimethylsilane, iodomethyldiethylmethylsilane, iodomethyldi-*n*-propylmethylsilane, iodomethyldi-*n*-butylmethylsilane and iodomethyldimethylphenylsilane. For comparison, polarograms were also registered for primary *n*-butyl iodide and primary isobutyl iodide. The polarograms were registered in 57% ethanolic solution at 25°. The Authors stated the method of preparation of the silanes employed. All the substances mentioned gave well-developed waves, the characteristic data of which were summarised in a table. Iodomethylphenyldimethylsilane gave a polarographic maximum. On addition of tetraethylammonium benzene sulfonate the curve was deformed and the maximum shifted, this disappearing on addition of gelatine. [Ot.So.]

95 – Reduction of complex cobalt ammoniates with negative substituents in the inner sphere on

the mercury drop electrode (in Russian). N. V. Nikolayeva-Fedorovitch and A. N. Frumkin (M.V.Lomonosov' State University, Moscow, U.S.S.R.). *Doklady Akad. Nauk S.S.S.R.*, 134 (1960) 1135–1137.
Solutions of 10^{-3} *N* $Co(NH_3)_4CO_3Cl$ in 0.1 *N* KCl were polarographed. Two waves were obtained, corresponding to the reduction of Co^{3+} to Co^{2+} and Co^{2+} to Co°. In reduction from the dilute solution a decrease in the current is observed on the first wave in the region of the zero-charge point. Formation of cobaltic hydroxide does not cause slowing down of the reaction, as is the case with $Co(NH_3)_6Cl_3$, since acidification with 10^{-3} *N* HCl does not change the shape of the curve. Slowing down is eliminated by addition of 0.1–1 *N* KCl. In the reduction of $[Co(NH_3)_4CO_3]^+$ a slowing down of the reaction is observed on transition from positive to negative surface charges. The same effect was also observed in the case of trans $[Co(NH_3)_4Cl_2]^+$ and $[Co(NH_3)_4NO_2]^+$.
[Ot.So.]

96 – Effect of complex ion formation in the polarographic reduction of arsenic(III) in hydrochloric acid. William H. Reinmuth and L. B. Rogers (Dept. of Chem., Mass. Inst. Technol., Cambridge, Mass., U.S.A.). *J. Am. Chem. Soc.*, 82 (1960) 802–805.
The authors have applied a slightly modified form of the theory of Koutecký to a study of the effects of complex formation on the polarographic reduction of arsenic(III). The rate of arsenic(III) reduction is controlled by the rate of electron transfer. The variation of $E_{1/2}$ with hydrogen ion and chloride ion concentrations was established. These results were compared with those expected for the rate-controlling step being the reduction of the complex species $As(OH)_2Cl$, $As(OH)Cl_2$, $As(OH)_2$, or $As(OH)_3$, using the data of Arcand. Agreement of theory with experiment was obtained for the case of $As(OH)Cl_2$. Possible mechanisms for the reduction of this species were cited; one likely mechanism involves chloride bridging. [Roy.Mur.]

97 – Polarographic behaviour of anabasine (in Russian). S. G. Mairanovskii, N. V. Barashkova and F. D. Alashev (Institute of Organic Chemistry, Academy of Sciences, U.S.S.R.). *Zhur. Fiz. Khim.*, 35 (1961) 435–443.
The polarographic behaviour of anabasine has been investigated over a broad range of pH values. It is shown that of the three waves observed on the polarograms, the first is an adsorption prewave; the second is the principal wave of pseudo-reduction of anabasine; and the third corresponds to the irreversible catalytic evolution of hydrogen. The products of the reversible electrode process, corresponding to the first two waves, dimerize at the electrode so that the waves can be described by the equation: $E = E° - RT/F \ln i^{2/3}/(i_1 - i)$. The dimer slowly decomposes, regenerating anabasine and evolving molecular hydrogen. At $t > 55°$ the process takes place very rapidly, so that the pseudo-reduction wave assumes the character of the catalytic hydrogen wave. [Ot.So.]

98 – Polarographic studies on natural peptides. I. Polarography of oxytocin, lysine- and arginine-vasopressin in cobalt(II) ammonia–ammonium chloride solutions. Hiroshi Sunahara, Darrell N. Ward and A. Clark Griffin (University of Texas M. D. Anderson Hospital and Tumor Institute, Dept. of Biochem., Houston, Texas, U.S.A.). *J. Am. Chem. Soc.*, 82 (1960) 6017–6022.
In the presence of certain types of peptides, cobalt(II) ammonia–ammonium chloride solutions exhibit, in addition to the cobalt wave, several catalytic waves at more negative tensions (the "protein waves"). The occurrence of these waves depends on the presence of -S-S- or -SH functions in the peptide. The polarographic waves arising from the title compounds and the derivatives bis-(acetyl)-lysine-vasopressin and S,S'-bis-(benzyl)-lysine-vasopressin have been investigated. Up to four waves in addition to the cobalt wave were observed. The effect of peptide structure, peptide concentration, ammonia concentration, and D.M.E. mercury pressure on these waves has been studied. One of the waves apparently largely depends on the presence of an -S-S- bond, another on the presence of an amino group as well. The mercury pressure studies indicate that an adsorption process is important in the mechanism producing the waves. See also following abstract.
[Roy.Mur.]

99 – Polarographic studies on natural peptides. II. Polarography of oxytocin, lysine- and arginine-vasopressin in cobalt(III) ammonia–ammonium chloride solutions. Hiroshi Sunahara, Darrell N. Ward and A. Clark Griffin (University of Texas M. D. Anderson Hospital and Tumor Institute, Dept. of Biochem., Houston, Texas, U.S.A.). *J. Am. Chem. Soc.*, 82 (1960) 6023–6027.
The polarographic "protein waves" arising from the presence of the title peptides and the derivatives bis-(acetyl)- and S,S'-bis-(benzyl)-lysine-vasopressin in cobalt(III) ammonia–ammonium chloride solutions has been investigated. The effects of peptide structure, peptide concentration, D.M.E. mercury pressure, and ammonia concentration on the protein wave-height were studied. The presence of -S-S- bonds and protonated basic groups was shown to give rise to certain of these waves. Adsorption processes are also shown to be involved in the wave mechanism. The behavior

of the protein waves of these compounds is similar to that observed in cobalt(II) solutions. See also preceding abstract. [Roy.Mur.]

100 – Polarographic studies on sarcomycin. Keiji Ida (Meiji Seika Kaisha Ltd., Japan). *Bull. Agr. Chem. Soc. Japan*, 24 (1959) 12–15.
The assay of sarcomycin is not possible if it has not been previously purified. A solution of 25–500 mg of sarcomycin in 20 ml of 0.1 *N* HCl is passed through a column (30 cm × 1.5 cm) of Duolite S-30 in the H^+ form. After rinsing with 0.01 *N* HCl, the sarcomycin is eluted with methanol. A solution containing 21.014 g of citric acid and 11.69 g of NaCl in 1 l of dilute HCl (pH 2) is used to dilute the methanolic eluate to a known volume, and the polarogram is recorded, after removal of oxygen, from —0.5 to —1.5 V. [Gio.Ser.]

101 – Oscillopolarographic determination of quinine alkaloids. II. L. Molnár and E. Domková (Dept. Natural Compounds, Chem. Inst., Academy of Sciences, Bratislava, Czechoslovakia). *Chem. Zvesti*, 14 (1960) 21–31.
The shape of the oscillogram is related to the structure of the alkaloids. The idealised oscillogram is characterised by three incisions. The influence of substituents on these incisions has been investigated. Also the length of the chain of the substituent in the 6 position strongly affects the shape of the oscillographic curve. The oscillograms have been obtained both with one cycle on one drop, and on the dropping electrode in LiCl supporting medium.
Twelve different quinine derivatives have been studied, and calibration curves are given correlating the concentration of the quinine derivative with the depth of the incision. [Gio.Ser.]

102 – Polarography of tantalum–ethylenediaminetetraacetate complex. Robert E. Kirby and Henry Freiser (Dept. of Chem., University of Arizona, Tucson, Ariz., U.S.A.). *J. Phys. Chem.*, 65 (1961) 191.
A new complex of tantalum(V) and EDTA is reported to exist in concentrations up to 0.01 *M* in the pH range 3–6. These solutions also give waves due to the reduction of Ta(V) to Ta(IV) at the dropping mercury electrode. The half-wave tension was found to be independent of EDTA concentration, but dependent on pH. In the pH region 3.3–5.6 the half-wave value varies linearly from —1.23 to —1.36 V *vs.* S.C.E. [D.S.Ru.]

103 – The determination of zinc in indium and nickel. E. G. Towndrow, R. Hutchinson and H. W. Webb (Johnson, Matthey & Co. Ltd., Research Laboratories, Exhibition Grounds, Wembley, Middlx., Great Britain). *Analyst*, 85 (1960) 769–770.
(a) *Zn in In.* Dissolve 1 g sample in 20 ml of 1 : 1 HCl/H_2O and dilute to 250 ml. Place aliquot containing 10–50 μg Zn in small beaker, add 1 ml of $FeCl_3$ solution (containing 1 mg/ml Fe and purified by extraction with 0.01% dithizone) and evaporate to dryness on a water bath. Redissolve in a minimum of HCl, add 0.5 ml *n*-BuOH, transfer to column of cellulose (about 15 cm long by 2 cm diameter previously washed with 100 ml of *n*-BuOH/HCl mixture) and elute with *n*-BuOH/HCl until the yellow Fe band is completely eluted when Zn is in eluate. Transfer to 100 ml beaker. Rinse receiver with 15 ml EtOH then with 7 ml H_2O and add rinsings to eluate. Evaporate to small volume, transfer to 10 ml beaker and evaporate to dryness. Add 2 ml $HClO_4$ and evaporate to dryness. Dissolve residue in 5 drops 1 : 1 HCl/H_2O, transfer to 10 ml graduated centrifuge tube. Make slightly ammoniacal, dilute to 5 ml and add 5 ml base electrolyte solution (0.2 *M* NH_4Cl, 1.0 *M* NH_3, 0.1 *M* Na_2SO_3, 0.005% gelatine). Mix, spin and polarograph supernatant fluid using Cambridge polarograph and Univector.
(b) *Zn in Ni.* As for In, but add 10 mg of Co as $CoCl_2$ to initial solution. [P.O.Ka.]

104 – The polarographic determination of niobium in highly alloyed steels. D. J. Brindley (Anal. Development Section, Chemical Laboratory, Joseph Lucas (Gas Turbine Equipment) Ltd., Shaftmoor Lane, Birmingham 28, Great Britain). *Analyst*, 85 (1960) 877–883.
The method was based on solution of the steel in HCl, precipitation of rare earths by hydrolysis with H_2SO_3, fusion with KOH to convert Nb to $KNbO_3$ and solution in $EDTA/H_2SO_4$. Mo was removed by extraction with 8-hydroxyquinoline in benzene and Nb was estimated in the EDTA/H_2SO_4 solution directly by polarography ($E_{1/2}$ = —0.65 V *vs.* Hg anode).
1 g sample is dissolved in 50 ml warm HCl (sp.gr. 1.18). Add a slight excess conc. HNO_3 dropwise to complete oxidation. Evaporate to dryness and bake lightly. Dissolve residue in further 30 ml HCl and evaporate to 15 ml. Cool and add 150 ml saturated SO_2 solution with stirring. Boil 2–3 min. Dilute to 200 ml with water, add filter paper pulp and boil 2–3 min. Leave at least 30 min or preferably overnight. Filter through No. 504 Whatman paper and transfer precipitate to the paper. Wash well with warm HCl (5% conc.). Transfer to gold crucible, dry, heat to char paper and then ignite at 800° for few minutes and cool. Add 4 g KOH, heat gradually to 350–400°, taking not less than 3 min for complete fusion. Cool slowly and extract with 80 ml 2% KOH

solution stirring with polythene-covered rod. Transfer to 100 ml graduated flask and dilute to mark. Transfer 20 ml of filtered solution to 150 ml beaker, add 0.29 g EDTA and 70 ml H_2O. Adjust pH to 1.9 with 10% H_2SO_4. Boil gently 30 min. Cool, dilute to 100 ml. Extract 25 ml with 2 × 10 ml 0.1% 8-hydroxyquinoline in benzene, shaking 2 min each time. Filter portion of lower phase into polarograph cell, remove O_2 with N_2 and polarograph. Prepare standard addition by adding 14 mg pure Nb_2O_5 to a further sample of mixed oxides from 1g of steel and repeat the fusion and extraction procedure. [P.O.Ka.]

105 – Comportement spectral et acidité de l'acide croconique et de dérivés voisins. P. Souchay et M. Fleury (Laboratoire de Chimie P.C.B. IV, Faculté des Sciences, Paris, France). *Compt. rend.*, 252 (1961) 737.
L'article est consacré au comportement spectral de l'acide croconique (R). Les Auteurs font cependant appel à la polarographie et à l'électrolyse sur cathode de mercure pour transformer cet acide et étudier les spectres des formes réduites. En milieu HCl (10^{-1} *N*) le polarogramme est caractérisé par deux vagues de réduction correspondant au départ de deux electrons chacune: soit $R + 2\,H^+ + 2\,e \rightarrow RH_2$ et $RH_2 + 2\,H^+ + 2\,e \rightarrow RH_4$. Le composé RH_2 est obtenu par réduction à la tension de —0.4 à —0.5 V/E.C.S.; le second, RH_4, par réduction à la tension de —0.8 et —1.0 V/E.C.S. Ce composé RH_4 peut encore capter deux électrons ($E_{1/2}$ = —1.1 V/E.C.S.); cette réduction entraine l'apparition d'une boue norîatre au sein de la solution ou la formation d'une pellicule noire lorsque la cathode est en plomb ou en zinc.
Les Auteurs s'intéressent également au composé $RH(CO_2H)$ qui peut être réduit en $RH_3(CO_2H)$. [Bad.Lam.]

106 – Polarographic determination of tocopherols in vegetable oils (in Russian). V. I. Koltunova. *Trudy Vsesoyuz. Nauch. Vitamin. Inst.*, 6 (1959) 260–265.
The oil is saponified with methanolic KOH (2 *N*) in an atmosphere of N_2. The mixture is diluted with water, and the unsaponifiable part is extracted with ether. The ether solution is evaporated to dryness, and the residue dissolved in ethanol. The sterols are precipitated with digitonin and filtered off. The tocopherols are oxidised in the alcoholic solution with cerium nitrate (0.1 *N* in ethanol), extracted with ether, and the ether extract distilled. The residue is dissolved in ethanol, an aliquot containing 2 mg of tocopheryl quinones is diluted with acetate buffer pH 7 containing 10 ml 75% ethanol, the solution is gassed with N_2, and the polarogram is recorded. Soya bean oil contains 13.2% α-, 57% β- + γ- and 29.8% δ-tocopherol. The corresponding percentages in cotton seed oil are 43.9, 56.1 and 0, and in sunflower seed oil 92.2, 0 and 7.8. These results are in agreement with previous data in the literature. [Gio.Ser.]

107 – Relationships between polarographic constants and the structure of organic molecules. VI. E. Fornasari, G. Giacometti and G. Rigatti (Phys. Chem. Inst., University of Padua, Italy). *Ricerca sci.* (Suppl. No. 5, Contributi di Polarografia), 30 (1960) 261–267.
Half-wave tensions have been measured in 50% alcohol solutions at various pH's for 2-, 3- and 4-pyridine aldehydes and for 2- and 4-quinoline aldehydes, the extrapolated values being given at pH = 0. In alkaline media, in which a relationship can be established between $E_{1/2}$ and the energy of the lowest unoccupied π-orbital of the oxidized form, the predicted values are consistent with the experimental ones; an analogous correlation does not occur in acid solution. This behaviour is tentatively attributed to the formal charge on the N atom in acid media. See also following abstract. [Fr.Pan.]

108 – Relationships between polarographic constants and the structure of organic molecules. VII. G. Rigatti (Phys. Chem. Inst., University of Padua, Italy). *Ricerca sci.* (Suppl. No. 5, Contributi di Polarografia), 30 (1960) 309.
Eleven aromatic iodo compounds are studied at the dropping mercury electrode; the reduction mechanism appears to be in each case: $Ar\text{-}I + e \rightarrow Ar^{\cdot} + I^-$ the amount of irreversibility being always the same. A linear relationship is found between $E_{1/2}$ and the π-electron energy difference between the initial and the reduced states. Anomalies are found in the case of charged molecules, presumably due to a charge effect on the amount of irreversibility. See also preceding abstract. [Fr.Pan.]

109 – Determination of mercapto groups in myosin by amperometric titration (in Russian). Yu. M. Torchinskiĭ. *Ukrain. Biokhim. Zhur.*, 31 (1959) 589–595.
Crude rabbit myosin displays 78–79 μM of mercapto groups per gram protein when titrated with $AgNO_3$, while it displays only 57 if titrated with $HgCl_2$. A 9% increase of titratable mercapto groups is produced by denaturation with urea at 38°. This means that myosin contains mercapto groups inaccessible to heavy metal ions. EDTA does not change the number of mercapto groups accessible to the metal ions. Iodoacetate combines with 40% of the free mercapto groups at a

concentration of $1.77 \cdot 10^{-3}$ and with 67% at a concentration of $9 \cdot 10^{-3}$. These findings are discussed in relation to the adenosine triphosphatase activity of myosin. [Gio.Ser.]

110 – Indirect polarographic determination of nitrates in biological materials. E. Davìdkova and J. Davìdek (Central Research Inst. of the Food Industry, Prague, Czechoslovakia). *Z. Lebensm. Untersuch. u. Forsch.*, 111 (1960) 477–483.
The method is based on the nitration of 2,4-xylenol in strongly acid medium and on the distillation of the nitro compound produced. The steam distilled product is collected in 4 *N* NaOH and determined polarographically. In practice 5 ml of the nitrate solution and 20 ml of 85% H_2SO_4 are introduced into a 250 ml flask and 1 ml of 2% 2:4-xylenol in acetone is added with cooling. After 20 min the nitration is complete and the reaction mixture is steam distilled after dilution with 100 ml of water. The distillate is collected in 5 ml of 4 *N* NaOH. After about 45 ml have been distilled 0.5 ml of 0.5% gelatin solution are added and the solution is made upto volume and polarographed. Nitrite can be removed by distillation as the methyl ester, halides by precipitation with silver sulfate in 85% H_2SO_4. The method is very sensitive being based on a 6-electron reduction. The results obtained for different materials are reported and discussed. The agreement with the colorimetric method is good and the method can be used over a wide range of concentrations. [Gio.Ser.]

111 – Polarographic determination of amphenone B (3,3-di-(*p*-aminophenyl)-butane-2-one) and Su 4885 (2-nicotinoyl-2-(3-pyridyl)-propane). L. Stárka and I. Buben (Research Inst. of Endocrinol., Prague, Czechoslovakia). *J. Pharm. and Pharmacol.*, 12 (1960) 175–178.
Amphenone B and Su 4885 can be determined by measuring the diffusion current at the dropping mercury electrode in aqueous solution. The half-wave values are respectively —1.40 and 1.22 V *vs.* S.C.E., and the heights of the waves are proportional to the concentrations. [Gio.Ser.]

112 – Amperometric titration of phenazone with iodine chloride (in Russian). A. I. Gengrinovich, L. E. Korneva and A. M. Murtazaev. *Doklady Akad. Nauk U.S.S.R.*, (1959) 40–42.
Phenazone can be titrated amperometrically with 0.01 or 0.001 *N* ICl using a rotating platinum electrode (600 rev/min) as the cathode and the S.C.E. as the anode. The end-point is characterised by an increase in the current due to the discharge of I^+ at the cathode. The reaction is very rapid and the whole titration may be carried out in 2–3 min. The addition of 30% ethanol to the solution permits the determination of phenazone in the presence of salicylic acid by reducing the rate of iodination of the latter. The error of this method is between 0.1 and 0.5%. [Gio.Ser.]

113 – The use of the potentiostat in analytical practice (in Czech). F. Plesnivý (Research Inst. for Vacuum Electronics, Prague, Czechoslovakia). *Sklář a keram.*, 10 (1960) 107–108.
The use of a potentiostat for the separation and the polarographic determination of Cd, Ni and Zn in electrolytic copper and of Pb and Sn in alloys is described. Electrolytic copper is removed from the solution by constant tension electrolysis and the solution remaining is evaporated. The residue is dissolved in aqueous NH_3–NH_4Cl buffer and Cd, Ni and Zn are determined polarographically. With alloys, Pb is separated from a tartrate medium by electrolysis at 550 mV *vs.* S.C.E., while Sn is determined, after decomposition of the tartrate complex with conc. HCl, by electrolysis at 650 mV in the presence of hydrazine hydrochloride as a depolariser. [Gio.Ser.]

114 – Polarographic determination of titanium in titanium-organosilicon compounds (in Russian). E. A. Terent'eva and M. O. Korshun. *Khim. Nauka i Prom.*, 4 (1959) 415–416.
The sample containing 2–10 mg Ti is treated with 1.5 ml HF (1:5) and evaporated. The treatment is repeated and 3 ml conc. H_2SO_4 are added to the residue which is then evaporated until it fumes. After dilution to 100 ml with 70% H_2SO_4, and filtration to eliminate carbon, 30 ml are used for recording the polarogram. Oxygen is eliminated by passing N_2 for 15 min, 6 drops 1% gelatin solution being used for maximum suppression. The half-wave value is 0.37 V *vs.* S.C.E. and the optimal range is from 10^{-3} to 10^{-4}. A calibration curve is needed and this may be obtained from samples of metallic titanium. [Gio.Ser.]

115 – Polarographic determination of iodine in tellurium metal. V. T. Athavale, R. G. Dhaneshwar, S. V. Gulavane and M. S. Varde (Anal. Div., Atomic Energy Estab. Trombay, Bombay, India). *Anal. Chem.*, 33 (1961) 311–312.
The metal is dissolved in sulfuric acid and dichromate and refluxed for 1.5 h. After attaching a condenser which dips into an absorption solution consisting of 2 ml 1 *N* NaOH, 0.2 ml sodium bisulfite and 8 ml water, 5 g oxalic acid is added to the distilling flask and the iodine is distilled under a low stream of air until about 25 ml distillate have been collected. The distillate is concentrated to 2 ml, acidified with sulfuric acid and 0.5 ml 10% hydrochloric acid and 1 drop of a 10% solution of sodium nitrite added. The iodine is extracted with carbon tetrachloride which is then

back-extracted into an aqueous phase containing 1 ml *N* NaOH and 2 drops 10% sodium bisulfite solution. The aqueous phase is acidified with sulfuric acid, 8 drops bromine water are added and the solution concentrated to 2 ml. After transferring into a 10-ml volumetric flask and making alkaline by addition of 1 ml of 0.05 *M* borax, 1 ml of 1 *M* potassium chloride and 2 ml 0.1 *M* gelatine are added. After making up to the mark the iodate is determined polarographically in a tension range between —0.9 and 1.4 V *vs.* S.C.E. The accuracy is better than 4%. [Kl.Gr.]

116 – Polarographic method for parts per billion of copper and lead in catalytic reformer feedstocks. B. W. Samuel and J. V. Brunhock (B. P. Research Centre, Petroleum Div., British Petroleum Co., Ltd., Sunbury-on-Thames, Middlx., Great Britain). *Anal. Chem.*, 33 (1961) 203–205.
A Mervyn-Harwell square-wave polarograph is used for the simultaneous determination of copper and lead in concentrations below 20 p.p.b. in catalytic reformer feedstocks. The precision of the determination is such that duplicated runs do not differ by more than 2 p.p.b. for lead and 3 p.p.b. for copper. The procedure for a duplicate determination takes 4 h for one analyst. The possibilities of contamination are discussed. The degree of reliability is shown in several tables. The procedure for the determination of copper and lead in typical naphtha from Middle East Crude oil is described in detail. [Kl.Gr.]

117 – Continuous polarographic determination of alpha-amino acids. W. J. Blaedel and J. W. Todd (Chemistry Dept., University of Wisconsin, Madison, Wis., U.S.A.). *Anal. Chem.*, 33 (1961) 205 207.
Alpha-amino acids are determined continuously by passing the sample through a chromatographic column. The sample stream is neutralized and buffered and is then passed through a small copper phosphate tube. The amino acids form a chelate with the copper and carry a proportional part of the copper out of the column. The copper–amino acid chelates are converted into the more stable copper–EDTA chelate. The stream is deaerated and the copper is determined polarographically. The relative standard deviation of the procedure is about 3%. Standardization can be performed with any alpha-amino acid. The mixing compartment and the copper phosphate column are described in detail. The preparation of the copper phosphate is given. The procedure and effluent rates of the columns are described. [Kl.Gr.]

118 – The polarography of quaternary ammonium compounds. B. C. Southworth, R. Osteryoung, K. D. Fleischer and F. C. Nachod (Sterling Winthrop Research Inst., Rensselaer, N.Y., U.S.A.). *Anal. Chem.*, 33 (1961) 208–212.
The products of the electrolytic reduction of several quaternary ammonium compounds have been identified. Two types of reaction are found and discussed: (1) the quaternary ion of simple aliphatic quaternaries acquires an electron to form a neutral entity which reacts with water to liberate hydrogen and forms the hydroxide of the compound; (2) the neutral entity breaks down into a tertiary amine and a hydrocarbon or two molecules rearrange to form a bis compound. The latter is found in those compounds having either an aromatic or a pyridinium group respectively. The polarographic procedure for analysis is limited to those compounds whose reduction tension is less negative than —1.9 V. At more negative tensions large irregular current changes are caused. [Kl.Gr.]

119 – Amperometric titration of sulfhydryl and disulfide groups with organic mercury compounds at the rotating mercury indicator electrode. W. Stricks and K. S. Chakravarti (Dept. of Chem., Marquette University, Milwaukee 3, Wis., U.S.A.). *Anal. Chem.*, 33 (1961) 194–199.
The procedure is given for the rapid determination of traces of sulfhydryl in amino acids, peptides and proteins with ethyl mercury chloride as titrant. The method allows the determination of 6–120 μg of sulfhydryl in biological materials in aqueous solution with an accuracy of ±0.5%. The procedure is described in detail. Under the experimental conditions stated disulfide reacts with sulfite according to $RSSR + SO_3^{2-} = RS^- + RSSO_3^-$. On addition of ethyl mercury RS^- reacts with the ethyl mercury compound and the reaction with sulfite goes to completion. The effect of pH and various buffer systems is studied. [Kl.Gr.]

120 – Theory of stripping voltametry with spherical electrodes. W. H. Reinmuth (Dept. of Chem., Columbia University, New York, U.S.A.). *Anal. Chem.*, 33 (1961) 185.
A theoretical discussion is given of stripping voltametry with spherical electrodes. Two sources of deviation from planar electrode behavior can be distinguished, *i.e.*, curvature and finite electrode volume. The former is the more important under usual experimental conditions. Formulas for spherical corrections for chronopotentiometry and hanging-drop polarography are given and their applicability discussed. See also following abstract. [Kl.Gr.]

121 – Stripping analysis with spherical mercury electrodes. I. Shain and J. Lewinson (Chem. Dept., University of Wisconsin, Madison, Wis., U.S.A.). *Anal. Chem.*, 33 (1961) 187–189.

The concentration distributions of metal within a hanging mercury drop electrode, which result from the processes taking place during the pre-electrolysis step of a stripping analysis are considered. The concentration is shown to be relatively uniform and an equation by which it can be calculated is derived. The theoretical current–voltage curves of the process can be calculated by combining the equations evaluated with the theory of Reinmuth. The theoretical and experimental curves are compared for the stripping of thallous ions. The stirring process in the pre-electrolysis step must be carefully controlled and timed. The theory adequately predicts the shape and magnitude of the experimental current–voltage curve. See also preceding abstract. [Kl.Gr.]

122 – Polarography of Ti(IV) and Zr(IV) in methanol and water–methanol solutions (in Italian). P. Desideri and F. Pantani (Anal. Chem. Inst., University of Florence, Italy). *Ricerca sci.*, 30 (1960) 2000–2008.
A well-defined polarographic step around —0.4 V/S.C.E. is obtained with $TiCl_4$ in CH_3OH + LiCl supporting electrolyte; the diffusion current is proportional to the Ti concentration over the range 1–10 *mM*; the electrode process is a reversible 1-electron reduction to Ti(III). On increasing the amount of water in solution two steps are formed, owing to the presence of hydrolysis products; another step at —1.2 V/S.C.E. is due to the H^+ discharge.
In the same solution $ZrOCl_2$ yields an irreversible step, proportional to the Zr concentration, at —1.2 V/S.C.E., which increases on increasing the amount of water. Experimental evidence is given that the process at the dropping electrode consists only of the discharge of H^+ ions. [Fr.Pan.]

123 – Organic polarography and molecular structure (in Italian). G. Semerano and G. Giacometti (Phys. Chem. Inst., University of Padua, Italy). *Ricerca sci.* (Suppl. No. 5, Contributi di Polarografia), 30 (1960) 177–189.
General considerations are stated for the polarographically reducible organic compounds. The mechanism of the electrode process and the influence of experimental conditions are examined. A relationship is shown to exist between half-wave tension and molecular structure; the behaviour of carbonyl and halogen derivatives is especially examined. [Fr.Pan.]

124 – Polarographic study of corrosion and rust prevention (in Japanese). Jiro Kato, Yoshi Arai, Minoru Ohashi and Tomio Baba (The Nitto Institute of Chemical Research, Kamikizaki, Urawa City, Japan). *J. Electrochem. Soc. Japan*, 27 (1959) 394–397.
In a few investigations concerning polarization characteristics of metals in neutral solution, it was observed that oxygen was consumed by metals at local cathodes. The rate of oxygen consumption by various metals in an acetate buffer has been studied by P. Delahay *et al.* In the present investigation, the relationship between the oxygen consumption and the corroded iron was quantitatively examined by the polarographic method. The variation of the oxygen concentration was determined continuously from the wave height at two pre-selected tension values (—0.4 and —1.2 V *vs.* S.C.E.).
These results were then applied to test various rust preventive oils. The polarographic method is very useful for this test and the efficiency of the oils is numerically determined by this method. The polarographic results were compared with those of a humidity cabinet test. [Ta.Fu.]

125 – Determination of polarization at an amalgam anode by polarographic method (in Japanese). Fumio Hine, Masaru Okada and Shiro Yoshizawa (Dept. of Industrial Chem., Kyoto University, Japan). *J. Electrochem. Soc. Japan*, 27 (1959) 419–422.
The polarization of an amalgam anode in caustic soda solution is observed by the polarographic method. In the paper, the following five sets of experimental conditions are used:
(1) concentrated amalgam and dilute caustic soda (0.2% Na–Hg, 10% NaOH);
(2) concentrated amalgam and concentrated caustic soda (0.2% Na–Hg, 50% NaOH);
(3) comparatively dilute amalgam and concentrated caustic soda (0.0125% Na–Hg, 50% NaOH);
(4) sufficiently dilute amalgam and dilute caustic soda (0.00625% Na–Hg, 10% NaOH);
(5) sufficiently dilute amalgam and concentrated caustic soda (0.00625% Na–Hg, 50% NaOH).
In cases (1) and (2), the anodic polarization seems to be very small, so that the polarograms consist of perfectly straight lines, but in case (3) the polarogram deviates from a straight line over the high current density range, this deviation being considered to be due to the anodic overvoltage. When the amalgam is dilute as in cases (4) and (5), the anodic overvoltage becomes much larger and the limiting current can be seen on the polarogram. The above-mentioned phenomena are probably due to the delay of diffusion in the amalgam, and are hardly dependent upon the concentration of caustic soda.
The equation for the anodic reaction rate of amalgam is presented. [Ta.Fu.]

126 – Electrolytic reduction of sulfochlorides under controlled tension. II (in Japanese). Moriake Urabe and Kazuo Yasukochi (Faculty of Engineering, Kumamoto University, Kyushu, Japan). *J. Electrochem. Soc. Japan*, 27 (1959) 526–530.

The electrolytic reduction of *m*-benzene-disulfochloride and *m*-nitrobenzene-sulfochloride was studied under controlled tension. Suitable conditions for the electrolytic solution and the cathode tension were investigated for the preparation of some intermediate products from these compounds. The intermediate products investigated were: *m*-benzene-disulfinic acid, *m*-C_6H_4-$(SO_2H)_2$; diphenyl-bis-disulfoxide, C_6H_4: $(SO_2\text{-}S)_2$: C_6H_4; bis-phenyl-1,3-bis-disulfide, C_6H_4 : $(S\cdot S)_2$: C_6H_4; *m*-nitrobenzene-sulfinic acid, *m*-NO_2-C_6H_4-SO_2H; *m*-aminobenzene-sulfinic acid, *m*-NH_2-C_6H_4-SO_2H; *m*-aminobenzene-disulfoxide, *m*-NH_2-C_6H_4-SO_2S-C_6H_4-NH_2; and *m*-aminobenzene-disulfide, *m*-NH_2-C_6H_4-S-S-C_6H_4-NH_2. A polarographic technique was applied for the determination of suitable cathode tensions. [Ta.Fu.]

127 – Polarographic behavior of indium in potassium iodide solutions (in Japanese). Teiichi Matsumae (Government Industrial Research Inst., Nagoya, Japan). *J. Electrochem. Soc. Japan,* 27 (1959) 549–552.

The polarography of indium in a solution of KI supporting electrolyte has been investigated. $E_{1/2}$ for indium in 0.1 *N* and 1 *N* KI solution was —0.537 V and —0.562 V *vs.* S.C.E., respectively. The slope of the wave in the presence of suitable quantities of gelatine corresponded closely to a reversible 3-electron reduction. The limiting current was proportional to the square root of the height of the mercury column and the temperature coefficient was 1.37% (in 1 *N* KI) and 1.39% (in 0.1 *N* KI).

The difference between $E_{1/2}$ for cadmium and indium was 0.18 V in 1 *N* KI solution and simultaneous determination of these metal ions would seem to be possible.

The formula of the complex was InI^{2+} when the concentration of iodide was less than about 0.5 *N* and InI_2^+ when it was more than 0.5 *N*. [Ta.Fu.]

128 – Polarographic method for the simultaneous determination of indium and cadmium (in Japanese). Teiichi Matsumae (Government Industrial Research Inst., Nagoya, Japan). *J. Electrochem. Soc. Japan,* 27 (1959) 604–607.

A polarographic method for the simultaneous determination of indium and cadmium has been established. The recommended supporting electrolytic solution contains 1 *N* KI and 0.015% gelatin. In this solution, the difference between the $E_{1/2}$ of indium and that of cadmium is 0.18 V and the limiting currents of these elements are proportional to their concentrations. The influence of various ions was investigated. In the presence of sulfate ion, the diffusion current of indium decreases and $E_{1/2}$ shifts to more negative values. Nitric ion and chloride ion do not interfere when the concentration of KI is 1 *N*. The effect of ferric iron can be removed by reducing it to the ferrous state with hydroxylamine. Microquantities of lead are soluble in KI solution as PbI_4^{2-} which is reduced at a potential approximately equal to that of indium. Therefore lead must be removed. Good results were obtained in the practical application of this method to the analysis of the byproduct from a zinc refining factory. [Ta.Fu.]

129 – The zinc complexes of α-amino acids (in Japanese). Yasushi Mashiko, Noboru Hosoya and Minoru Akimoto (Hot Spring Research Center and Phar. Inst., Nihon University, Japan). *J. Electrochem. Soc. Japan,* 27 (1959) 100–103.

The stability constants and compositions of several zinc complexes of α-amino acids have been investigated by a polarographic method. In the pH range of Sörensen and Kolthoff buffers, the $E_{1/2}$'s of the glycine, L-glutamic acid, DL-methionine and L-histidine complexes of zinc vary with pH according to the relations derived from the view-point of the theory of absolute reaction rate for irreversible processes. The reduction of these zinc complexes is irreversible. The coördination number of the zinc complexes of these amino acids is 2 in the presence of excess amino acid. The stability constants were determined for glycine (9.3), L-glutamic acid (9.0), DL-methionine (8.3) and L-histidine (11.2). [Ta.Fu.]

130 – Polarography of $ZnCl_2$ in molten Na_3AlF_6 bath, with use of vertically vibrating platinum micro-cathode (in Japanese). Hidehiko Kido, Tsunesato Rokujo and Yasmasa Hayakawa (Dept. of Chem., College of Liberal Arts, Saitama University, Urawa, Japan). *J. Electrochem. Soc. Japan,* 27 (1959) 24–26.

The cathodic limiting current of $ZnCl_2$ in a molten Na_3AlF_6–CaF_2 bath at a vertically vibrating platinum micro-cathode is studied. The effects of bath temperature, frequency and the amplitude of vibration of the cathode on the limiting current are investigated. The linear relationship between the cathodic limiting current and the concentration of zinc chloride was obtained under suitable conditions. The half-wave value was about 1 V *vs.* a platinum anode.

The diffusion coefficient of the zinc ion in the fused system was calculated as $5\cdot10^{-6}$ cm/sec. [Ta.Fu.]

131 – The polarographic catalytic wave of proteins in tris-(ethylenediamine)-cobalt(III) chloride

solution (in Japanese). (Chem. Lab., Faculty of Fisheries, Prefectural University of Mie, Mie Prefecture, Japan). *J. Electrochem. Soc. Japan*, 27 (1959) 78–82.
The polarographic effect of proteins on the tris-(ethylenediamine)-cobalt(III) chloride wave has been studied. In ammoniacal buffer, the complex showed a single wave in the presence of egg white lysozyme, horse serum albumin, amylase, ovalbumine and casein at a tension of about —1.55 V *vs.* S.C.E. The height of the wave decreased with decrease of the cystine content of the protein. Similar protein single waves were also obtained in the veronal of the Tris buffer containing $Co(en)_3Cl_3$. In the ethylenediamine–ethylenediamine hydrochloride solution, a slightly deformed protein single wave was observed. It was concluded that the protein single wave is a catalytic wave and that its electrode process is similar to those of the protein double waves. [Ta.Fu.]

132 – The effect of supporting electrolyte and interfacial active substance on the a.c. polarogram. Studies using a pen recording a.c. polarograph (in Japanese). Mitsugi Senda, Mitsuko Senda and Isamu Tachi (Dept. of Agriculture, Kyoto University, Japan). *J. Electrochem. Soc. Japan*, 27 (1959) 83–88.
The behavior of a.c. polarograms obtained using a pen recording a.c. polarograph of the bridge type has been investigated and the effect of the supporting electrolyte and surface-active substance on the a.c. waves has been studied.
The response of the recorder to a parallel resistance–capacitance network was examined and it was shown that the measured value of the a.c. wave is related to the equivalent electrode admittance by the equation $i_{a.c.}$(in mho) $= 1/R_e' + \theta W C_e'$ where θ is a characteristic constant of the recorder. The value of K defined by $K = i_s/i_d n\sqrt{\tau}$ (i_s: peak current, i_d: diffusion current, n: number of electrons, τ: drop time) was obtained for the electrode reaction. The values of K for Tl and Pb in KCl, and those for Zn in KI, KCNS, KBr, KCl and KNO_3 were measured. From these measurements, the reductions of Tl and Pb in KCl were shown to be reversible. The effect of the surface-active substance, Tween T, and the effect of active charcoal on the a.c. wave was also examined. The decrease of the wave-height corresponding to the reversibility occurred stepwise on addition of the active substance. [Ta.Fu.]

133 – The polarographic reduction of benzal aniline (in Japanese). Shin-ichi Ono and Miyoshi Uehara (University of Osaka Prefecture, Japan). *J. Electrochem. Soc. Japan*, 27 (1959) 93–96.
The polarographic reduction of benzal aniline (B) has been studied in non-aqueous media and in various buffer solutions. The reduction mechanism was investigated by the technique of controlled tension electrolysis. In the non-aqueous medium containing aniline, ethanol and glacial acetic acid with tetramethyl ammonium bromide as supporting electrolyte, B shows one well-defined reduction wave, the height of which is proportional to the concentration of B. This wave corresponds to a 2-electron reduction leading to benzyl aniline. $E_{1/2}$ is —0.85 V *vs.* S.C.E. at pH 5.0 and —0.85 V at pH 8.2. In buffer solutions ($6 <$ pH < 10) B gives two waves. The height of the first wave, which is a 1-electron reduction producing the aniline benzyl radical, decreases with time owing to the hydrolysis of B. On the other hand, the height of the second wave, which is the overlap of the reduction wave of benzal aldehyde produced by hydrolysis of B with the 1-electron reduction wave of the anilinobenzyl radical to benzyl aniline, increases and thus the total wave-height remains constant. $E_{1/2} = -0.075$ pH-0.400 V (1st wave) and $E_{1/2} = -0.068$ pH-0.902 V (2nd wave). [Ta.Fu.]

134 – The use of the abnormal copper wave at the rapidly dropping mercury electrode for the study of maximum suppressors (in Japanese). Masayoshi Ishibashi, Taitiro Fujinaga and Masanori Sato (Chem. Inst., Faculty of Science, University of Kyoto, Japan). *J. Electrochem. Soc. Japan*, 27 (1959) 96–98.
The abnormal wave of Cu ions in a supporting electrolyte consisting of non-complexing agents in the presence of various surface-active substances (SAS) has been studied. In general, the minimum occurs in the tension range 0 to —0.8 V *vs.* S.C.E. and is most evident at the tension of the electrocapillary maximum. Perchloric, nitric, sulfuric and phosphoric acids are investigated as supporting electrolytes. Each acid has a different amount of effect on the polarographic wave of Cu. Generally, the abnormality becomes more evident with increasing hydrogen ion concentration and with increasing concentration of SAS. The tensions of the adsorption and desorption of the SAS on the mercury electrode were determined by the tensammetric technique or from the conventional polarogram at the rapidly dropping mercury electrode (RADME) with a drop time of the order of a few tenths of a second. The following were recorded: (1) the residual current curve of 1 M $NaClO_4$ in the presence of SAS at the RADME; and (2) the polarogram of 1 mM Cu ions in 1 M $HClO_4$ solution in the presence of more than 0.01% SAS. If the first polarogram shows no adsorption–desorption wave over the whole tension range upto the final current rise of the supporting electrolyte and if the second polarogram shows the normal Cu wave, then the SAS can be regarded as an ideal maximum suppressor for polarographic analysis. From the experiments it was found that polyacrylamide fulfils the above two requirements. [Ta.Fu.]

135 – Effect of certain surface-active organic cations on the reduction kinetics of the IO_3^- ion at a dropping mercury electrode (in Russian). V. I. Zykov. *Zhur. Fiz. Khim.*, 35 (1961) 355–362.
The effect of additions of the cations $(C_2H_5)_4N^+$ and $(C_4H_9)_4N^+$ on the reduction kinetics of the iodate ion in the presence of some alkaline and alkaline earth metal cations and of La^{3+} has been investigated. The experimental results obtained have been interpreted in terms of earlier developed concepts as to the role of ion pairs in the electroreduction of ions of the type XO_3^-. [Ot.So.]

136 – Kinetics and mechanism for the electrochemical reduction of benzophenone in acidic media. Makoto Suzuki and Philip J. Elving (Dept. of Chem., University of Michigan, Ann Arbor, Mich., U.S.A.). *J. Phys. Chem.*, 65 (1961) 391–398.
The kinetic and mechanism factors in the electrochemical reduction of ketones have been investigated by examining the reduction of benzophenone and *p*-bromobenzophenone over the pH range 2 to 7. The wave I electron process is quite rapid, but the subsequent irreversible chemical process causes the net reaction to appear irreversible. The process producing the second one-electron wave is quasi-reversible. The combined wave observed above pH 5 is controlled at first by the wave II process, but with increasing pH the control shifts to the wave I process. [D.S.Ru.]

137 – Polarographic and coulometric investigations on the reduction rate of cobalt(II) in the presence of cystine (in English). Emilian B. Weronski (Dept. of Chem., University of Warsaw, Poland). *J. Phys. Chem.*, 65 (1961) 564–565.
In considering the increase of the diffusion current previously reported in cobalt solutions, experiments were carried out to re-examine the current of cobalt ions in the presence of cystine. The results suggested that the phenomenon is due to an increase in the reduction rate of the cobalt II ions. [D.S.Ru.]

138 – Quantitative determination of vanillin and ethyl-vanillin in some sweet-products (vanillin sugar, puddings, etc.) (in German). H. Woggon and K. Rauscher (Akad. Wiss. Berlin, Inst. Ernähr, Potsdam-Rehbrücke, Deutschland). *Nahrung*, 3 (1959) 161–173.
Oscillo-polarographic determinations are possible within ±10% by using a special cell (for details, see the text) and the following procedure: the sample (0.1–0.25 g for a content of 0.1–1%) is made up to 25 ml with semicarbazide (0.5 *M* in 0.1 *N* HCl) and then polarographed, filtration and elimination of oxygen being unnecessary. The results are read from a calibration curve, care being taken to keep all the experimental conditions constant (such as the capillary, the Hg level, etc.). [Ca.Cas.]

139 – Study of the reduction waves of the isomers of nitrophenol by means of the alternating current polarograph. T. Takahashi and H. Shirai (Inst. Ind. Sci., Univ. Tokyo, Japan). *Talanta*, 8 (1961) 177–186.
In a study of the a.c. polarography of *o*-, *m*- and *p*-nitrophenols it was found that the wave heights were proportional to the concentrations of the nitrophenols in potassium hydroxide and ammonium chloride–ammonium hydroxide base solutions. The reduction waves for direct current polarograms however are not always diffusion-controlled. *p*-Nitrophenol in 1 *N* potassium hydroxide solution has its first peak at —0.915 V and a second at —L.45 V. The first wave height is independent of the concentration of potassium hydroxide and of the added salts. It is free from kinetic current. The first peak height of *m*-nitrophenol was found to be equal to that of *p*-nitrophenol under similar conditions at —0.78 V, and independent of the potassium hydroxide concentration. From the d.c. polarograms in different potassium hydroxide solutions, it is evident that they can be contaminated by the kinetic current. *o*-Nitrophenol shows in 1 *N* potassium hydroxide a single peak at —0.92 V, which is lower than that of either *p*- or *m*-nitrophenol. In 0.1 *N* potassium hydroxide however two distinct peaks were formed (at —0.88 and at 1.01 V). The d.c. polarogram of *o*-nitrophenol is independent of the kinetic current only at a pH above 9. [Ja.Inc.]

140 – Amperometric titration with two indicator electrodes and allied techniques. J. T. Stock (Dept. of Chem., University of Connecticut, Storrs, Conn., U.S.A.). *Microchem. J.*, 3 (1959) 543–555.
A review of the more recent applications of the "dead-stop end-point" titration methods, now generally known as amperometric titration, with two indicator electrodes is given. The apparatus and techniques and inorganic and organic applications are discussed. Such techniques are very sensitive and the electrode systems simple. Their application to the microchemical field willbe of great value in the future. (90 references). [Gio.Ser.]

141 – Polarography of organic halogen compounds. I. Steric hindrance and the half-wave potential in alicyclic and aliphatic halides. Frank L. Lambert and Kunio Kobayashi (Dept. of Chem., Occidental College, Los Angeles, Calif., U.S.A.). *J. Am. Chem. Soc.*, 82 (1960) 5324–5328.

The polarographic half-wave values of a series of cycloalkyl and straight and branched-chain alkyl bromides have been determined in N,N-dimethylformamide. The reductions are irreversible and give a single wave. The qualitative correlation between ease of reduction and S_N reactivity of these compounds is discussed from the viewpoint of steric requirements for backway attack by the electrode. Consideration is also given to the effect of the size of the "attacking group" (the electrode) on the ease of reduction. [R.Mur.]

142 – Polarographic behavior of alkyl phenyl ketones with nuclear and sidechain halogen substituents. Philip J. Elving and Joseph T. Leone (University of Michigan, Ann Arbor, Mich., and Pennsylvania State University, University Park, Pa., U.S.A.). *J. Am. Chem. Soc.*, 82 (1960)5076–5080.
The polarographic behavior of a number of substituted acetophenones has been investigated. The effect of the position of the chlorine or bromine substituents (in the benzene ring and/or in the methyl group) on the half-wave reduction values of the carbonyl group and halogen was studied over a wide range of pH. Nuclear halogen substitution facilitates carbonyl reduction, the order of ease of reduction being 2,5-chloro- > 4-bromo- > 4-chloro- > acetophenone. Reduction of the nuclear halogen was not observable because of buffer discharge. Reduction of alkyl substituted halogen (bromo- easier than chloro-) occurred at electric tensions lower than those for carbonyl reduction, and the $E_{1/2}$ for carbonyl reduction was thus not noticeably affected by the presence of side chain halogen. The ease of alkyl halogen reduction was not measurably influenced by nuclear halogen substitution in the *para*-ring position (presumably because of weakened inductive effects) and the reduction was pH dependent in acid solutions. This pH dependency was interpreted in terms of the hydrogen being involved in a push-pull mechanism at the electrode surface. Hydrolysis of the methyl halogen (particularly bromine) complicated the study in alkaline regions. [R.Mur.]

143 – Polarographic behaviour of nitro and nitrosoguanidine. Gerald C. Whitnack and E. St. Clair Gantz (General Research Branch, U.S. Naval Ordnance Test Station, China Lake, Calif., and Aircraft Gas Turbine Division, General Electric Co., Cincinnati, Ohio, U.S.A.). *J. Electrochem. Soc.*, 106 (1959) 422–427.
The polarographic behaviour of nitro- and nitrosoguanidine has been investigated in various alkaline, neutral and acidic solutions. The possible reduction mechanisms are discussed and the optimum conditions for the determination of the nitroso compounds in the presence of the nitro compound, and for the reduction of the nitro compound are stated precisely. Half-wave values of tension, diffusion current constants and *n*-values are given and the multiple waves, observed under certain pH conditions, discussed. [Fe.Jol.]

144 – Polarographic study of the desulphination of cysteine sulphinic acid by oat leaves extracts (in French). P. Fromageot and U. Patino-Bun (Service de Biologie, Commissariat à l'Energie Atomique, Centre d'Etude Nucl. de Saclay, Gif-sur-Yvette, France). *Biochim. Biophys. Acta*, 46 (1961) 533–544.
The polarographic determination of sulphite in the presence of cysteine sulphinic acid, an α-ketonic compound and an enzymic preparation from oat leaves can be carried on in a cell maintained at 37° using the anodic oxidation wave of sulphite. A dropping mercury electrode connected to a recording polarograph is used and a S.C.E. serves as the comparison electrode. No tension is applied to the electrodes and the current is recorded.
By this technique the rate of transamination of cysteine sulphinic acid has been studied and the results are reported and discussed. [Gio.Ser.]

145 - Effect of structure on the stereochemistry of electrode reactions. P. J. Elving, I. Rosenthal, J. R. Hayes and A. J. Martin (University of Michigan, Ann Arbor and Pennsylvania State Univ.. University Park, Pa., U.S.A.). *Anal. Chem.*, 33 (1961) 330.
The polarographic reduction of monobromo-C_4-dibasic acids and esters, such as monobromomaleic and monobromofumaric acids and their diethyl esters is described. The reduction products are identified on the microscale by polarographic and coulometric methods and on the macro scale by isolation. Two electrons are consumed for the reduction process. The reduction mechanism of the compounds is explained and equations are proposed. The influence of varying the pH of the solution is studied and half wave values for a large number of pH values are given. [Kl.Gr.]

146 – Voltametric determination of cobalt and nickel in hard magnetic alloys. R. D. DeMars I.B.M. Research Center, Yorktown Heights, N.Y., U.S.A.). *Anal. Chem.*, 33 (1961) 342.
The method describes a rapid and accurate determination of cobalt and nickel in magnetic alloys. The samples are analyzed at the hanging drop electrode. A three-electrode system is used, similar

to that described by Shain and Svoboda. The rate of voltage change is 33,3 mV per sec. A general purpose voltametric instrument is used in combination with a Sargent recorder. The area of the mercury drop is 0.0757 sq.cm. A pyridine–potassium chloride supporting electrolyte is used. The procedure for standard solutions is: 2–20 ml of 10^{-2} *M* Ni and Co solution is placed in a 200 ml volumetric flask. 2.98 g potassium chloride are added and 1 ml pyridine. After dissolution the pH is adjusted to 6 and made up to the mark. After deaeration for 15 min with nitrogen a part is analyzed by the common voltametric procedure. The average deviation is in most cases below 1%. [Kl.Gr.]

147 – Polarographic determination of nitrite and nitrate. R. Annino and J. E. McDonald (Chem. Dept., Canisius College, Buffalo 8, N.Y., U.S.A.). *Anal. Chem.*, 33 (1961) 475.
Nitrite can be determined with minimum difficulty in a supporting electrolyte containing a citric acid–sodium citrate buffer of pH 2. Nitrate is determined after the removal of the nitrite by reaction with hydrazoic acid according to the method of Kolthoff in a supporting electrolyte which contains uranyl ion. The diffusion current of nitrite is measured at —1.2 V *vs.* S.C.E. The decrease in current is about 1% in 5 min which is mainly due to disproportionation. The deviation in the nitrate determination is in most cases below 1%, and in the determination of nitrite below 2.5%. An analysis of both nitrite and nitrate takes about 30 min. [Kl.Gr.]

148 – Polarographic determination of sulphur and sulphur-containing compounds in petroleum and petroleum products and of metallic dust in used oils (in German). G. R. Schultze and W. Irion (Hannover, Germany). *Angew. Chem.*, 73 (1961) 147.
Nur eine kurze Zusammenfassung des Vortrages, abgehalten anlässlich der Arbeitstagung *Moderne Methoden der Analyse organischer Verbindungen*, in München (1960 Oktober).
Gemäss den mit verschiedenen Lösungsmittelgemischen erhaltenen Untersuchungsergebnissen lassen sich elementarer Schwefel, Polysulfiden, Mercaptanen, Sulfiden, Disulfiden in Erdölen polarographisch bestimmen. Nach Veraschung und Aufschliessung ist ferner die Bestimmung sämtlicher Abriebsmetalle ist ferner die Bestimmung sämtlicher Abriebsmetalle nebeneinander in gebrauchten Altölen möglich. [Ja.Inc.]

149 – Polarography of sulphur-containing proteins (in German). W. Lamprecht and H. Katzmeier (München, Germany). *Angew. Chem.*, 73 (1961) 148.
Kurze Zusammenfassung des Vortrages, anlässlich der Arbeitstagung, *Moderne Methoden der Analyse organischer Verbindungen*, in München, (1960 Oktober).
Es wurde festgestellt, dass Disulfidgruppen enthaltende Proteine katalytische Wasserstoffwellen geben. Die typische "SH-Enzyme" können jedoch polarographisch als *p*-Chloromercuribenzoat-Komplexe gemessen werden. Durch Zusatz von Harnstoff gelingt es zwischen maskierten und freien Sulfhydryl- oder Disulfidgruppen an Enzymen zu differenzieren. [Ja.Inc.]

150 – A polarographic study of *d*-glucuronolactone. R. J. Thibert and A. J. Boyle (Dept. Chem., Wayne State Univ., Detroit, Mich., U.S.A.). *Talanta*, 7 (1961) 175–180.
The polarographic behaviour of *d*-glucuronolactone in various supporting electrolytes and maximum suppressors was investigated. It was found that the diffusion current shows a linear relationship to the concentration of *d*-glucuronolactone in lithium chloride and potassium chloride as supporting electrolytes in the range of 10–100 µg/ml. Using 0.02 *N* lithium chloride and 0.005% gelatine the half-wave value is —1.60 V *versus* the mercury pool. Ammonium chloride as a supporting electrolyte was not found to be suitable. The use of any standard buffers suppressed the wave. Pyruvate interferes, whereas *d*-glucose does not. [Ja.Inc.]

151 – The anion-exchange separation of tin, antimony, lead and copper. M. Ariel and E. Kirowa (Faculty of Sci., Dept. Chem., Israel Inst. Technol., Haifa, Israel). *Talanta*, 8 (1961) 214–222.
A method is described in which tin, antimony, lead and copper can be separated using an Amberlite IRA-400 (100–140 mesh) anion exchange resin column (200 mm long, with diameter of 3 mm). The eluents are the following: 7 *N* HCl for Pb; 1.56 *N* HCl for Cu; 0.3 *N* HCl + 1 *N* HF for Sb; and 6 *N* NaOH for Sn, used in this order.
Lead was determined polarographically using 1 *N* NaOH solution as supporting electrolyte. Antimony was determined by potentiometric titration with potassium bromate. For elimination of oxide film formation on the platinum electrode, it was previously immersed in a reducing (iron(II)sulphate) solution for 15 min. Tin was determined polarographically in a supporting electrolyte being 3 *N* for sodium chloride and 1 *N* for hydrochloric acid, with 0.001 %Triton X-100 present as maximum suppressor. Copper was determined spectrophotometrically employing ferrocyanide.
The method is adapted to the analysis of alloys. [Ja.Inc.]

152 – Polarographic reduction of some aliphatic ketones. R. M. Powers and R. A. Day, Jr. (Chem. Dept., Emory University, Atlanta 22, Ga., U.S.A.). *J. Org. Chem.*, 24 (1959) 722–724.
The following compounds have been studied: acetone; methyl-cyclopropyl-ketone; 1-phenylpropanone-2(I); 1,3-diphenylpropanone-2(II); 1,1,3-triphenylpropanone-2(III); 1,1,3,3,-tetraphenylpropanone-2(IV); and 2,2,4,4-tetraphenyl-3-oxoetanone (V). A Leeds and Northrup Electrochemograph type E was used, the comparison electrode being of the Hg-tetrabutylammonium chloride (1 *M*) type; half-wave values were corrected for the IR drop, galvanometer damping lag and tension of the above electrode against a S.C.E. As the supporting electrolyte, 0.05 *M* tetrabutylammonium chloride in dioxane: water (75 : 25) or 0.1 *M* tetrabutylammonium chloride–0.1 *M* tetrabutylammonium hydroxide in alcohol–water (80 : 20) were used; the concentration of the ketone to be studied was kept at 0.001 *M*. $E_{\frac{1}{2}}$ values were tabulated; they range from —2.61 V (in dioxane–water) or —2.53 V (in alcohol–water) for acetone to —2.13 V (resp. —2.05 V) for IV; V gives two slightly separated waves, at approximately —2 V.
Inconclusive data were obtained on the number of electrons involved in the processes; macroelectrolysis of II and IV show that there is no evidence of bimolecular reactions. [Ca.Cas.]

153 – Complex compounds of indium with trioxyglutaric acid (in Russian). N. K. Davidenko. *Zhur. Neorg. Khim.*, 5 (1960) 48–55.
The interaction of indium with trioxyglutaric acid was studied over a wide range of pH by means of electrochemical methods (potentiometric titration with measurements of pH, measurements of conductance, migration of ions in the electrolysis, polarography). In such a way it was found that cationic complexes ($InC_5H_6O_7{}^+$, $In_2C_5H_4O_7{}^{2+}$) are formed in acid solutions, the neutral complex $InC_5H_5O_7$ in weakly acid or neutral solutions, and the anionic complex $InC_5H_4O_7{}^-$ in basic solutions. The following compounds were isolated from the solutions: $InC_5H_5O_7 . 3H_2O$ and $NaInC_5H_4O_7 . 3H_2O$. [Li.Ne.Ro.]

154 – Effects of electrolytes and of gelatin on the half-wave potentials of carbon tetrachloride, dibromoacetate, and *p*-dinitrobenzene. Leif E. I. Hummelstedt and L. B. Rogers (Dept. of Chem. and Laboratory for Nuclear Science, Massachusetts Inst. Technol., Cambridge, Mass., U.S.A.). *J. Electrochem. Soc.*, 106 (1959) 248–253.
Media were chosen so that the reductions of each compound occurred on both sides of the electrocapillary maximum. The effect of capillary-active anions was to retard the less-cathodic reduction steps. The presence of capillary-active tetramethylammonium ions facilitated the second reduction step of both carbon tetrachloride and dibromoacetate ion. The capillary-inactive calcium ion had little effect on the halogenated compound, but it greatly facilitated the second reduction step of *p*-dinitrobenzene. This behaviour thus suggested ion-pair formation, with the known divalent intermediate. Gelatin, as expected, produced, under certain conditions of alcohol concentration, a shift of the second half-wave value to less-cathodic values. This effect only occurred in acidic media, when the reduction took place on the negative branch of the electrocapillary curve. Protonated gelatin in the double layer is thought to induce this effect. [Fe.Jol.]

155 – Polarographic determination of N-(5-nitro-2-furfurylidene)-1-amino-hydantoine (Furandantin Boehringer, F) (in German). J. Blazěk (Staatsanstalt Arzneimittelkontrolle, Prague, Czechoslovakia). *Pharmazie*, 14 (1959) 157.
The F tablets are powdered and a quantity corresponding to 100 mg of F is weighed and stirred with 100 ml of 0.1 *N* Na_2CO_3 solution; after uniform dissolution and standing, 0.5 ml of the clear solution are transferred to a cylinder and 0.5 ml of the standard solution (1 mg/ml of F in 0.1 *N* Na_2CO_3) and 19 ml of the 0.1 *N* Na_2CO_3 solution are added; another 0.5 ml aliquot of the sample solution is made up to 20 ml with the 0.1 *N* Na_2CO_3 solution. Polarograms of the two solutions, deareated by nitrogen, are run using a galvanometer sensibility of $4 \cdot 10^{-9}$ A/mm, a dropping mercury cathode ($t = 3$ sec) and a mercury anode. The F quantity is read off from a calibration curve constructed by using 0.5 — 2.0 ml of the above standard solution diluted to 20 ml with the 0.1 *N* Na_2CO_3 solution. [G.de An.]

156 – Detection of *sec*-β-oxyethylamines by fluorescence, polarography, paper chromatography and thermochromy (in German). K. H. König and H. Berg (Institut für Mikrobiologie und experimentelle Therapie, Jena, Deutschland). *Z. anal. Chem.*, 166 (1959) 92–100.
Benzoquinone-1,4 reacts with some *sec*-β-oxyethylamines to give asymmetric monobasic 2-substituted compounds which can be used for the characterization of the amines. The sec β-oxyethylamines are derived from the basic compound $RNHCH_2CH_2OH$, where R can be an aliphatic, arylaliphatic, aromatic or oxyalkyl radical; the β-hydrogen atoms in the ethyl radical can also be replaced. The characterization is performed in 20 — 40% ethanol solution. All the investigated compounds give polarograms involving a 2-step (2-electron) reduction and typical fluorescence colours. Polarographic runs are performed at pH = 6 (ethanolic Britton–Robinson buffer) with

the dropping mercury–normal calomel electrodes at 25°. The behaviour of the compounds in circular paper chromatography using acetone–water (5 : 1) as the moving phase is also discussed with respect to the possibility of detecting the bands in U.V. light and before or after (thermochromy) warming. By polarography it is possible to detect down to about $5 \cdot 10^{-6}$ g of the substance and by chromatography down to about to 10^{-6} g. The behaviour of some other different substituted primary and secondary aminocompounds is also reported. [G.de An.]

157 – Polarometric titration of thorium in monazite (in Chinese). Shao-Chun Tung and Er-Kang Wang (Institute of Applied Chem., Academia Sinica, China). *Acta Chim. Sinica*, 25 (1959) 37.
The sample is fused with KHF and the polarometric measurement is made at 0.75 V *vs.* S.C.E. in a solution containing $AlCl_3$ (1.5 *N*), CH_3COOH (7%) and CH_3COONa (pH 1.7). The error is ±2%. [G.de An.]

158 – Theory and application of the suppression of polarographic maxima. VI. Investigations of macromolecular condensation and of reaction kinetics (in German). I. Rusznák, I. Králík and K. Fukker (Research Institute of the Textile Industry and Institute of Practical Chem., Technical University, Budapest, Hungary). *Collect. Czechoslov. Chem. Communs.*, 26 (1961) 645–649.
The ability of pre-condensates of urea and formaldehyde and of partially split starch to suppress oxygen maxima has been investigated. In the former case it was found that the stability and therefore also the suppressing capacity are influenced by the pH of the pre-condensate. In the case of starch it was found that the initially inactive starch suppresses the maxima in an increasing amount with increasing time of splitting. [Ot.So.]

159 – Application of complexones in chemical analysis. LIV. Polarographic determination of cadmium in metallic indium (in English). M. Kopanica and R. Přibil (Laboratory of Anal.Chem., Inst. of Geochemistry, Academy of Sciences, Prague, Czechoslovakia). *Collect. Czechoslov. Chem. Communs.*, 26 (1961) 398–402.
Conditions have been found for the determination of traces of cadmium in metallic indium. The method is based on the displacement of cadmium from its complex with 1,2-diaminocyclohexane-N,N,N′,N′-tetraacetic acid by thorium nitrate. Indium is polarographically inactive under these conditions. The sample is dissolved in a minimum of $HClO_4$, and evaporated to near dryness. The residue is dissolved in water, the acidity decreased by a few drops of ammonia and the solution transferred to a 50 ml volumetric flask. 20 ml of a formate buffer pH 3 and 20 ml 0.5 *M* solution of CDTA are added. After addition of one drop of 1% xylenol orange solution a 10% thorium nitrate solution is added until the colour changes from yellow to red. The solution is made up to volume and a polarogram is recorded after removal of air from -0.2 to -1.0 V (S.C.E.). $E_{1/2}$ for Cd is about -0.60 V. A cell with an external calomel electrode was used in the experiments. Zn, Ni and Co are also displaced by thorium, their $E_{1/2}$ being however sufficiently distant from that of Cd. [Ot.So.]

160 – Polarography of non-benzenoid aromatic and related substances. VII. A polarographic study of the acid-base propecties of the tropylium ion. P. Zuman, J. Chodkowski and F. Šantavý (Polarographic Inst., Academy of Sciences, Prague, Czechoslovakia). *Collect. Czechoslov. Chem. Communs.*, 26 (1961) 380–391.
A single polarographic wave of $E_{1/2} = -0.3$ V is observed for the tropylium ion at concentrations lower than $1.5 \cdot 10^{-4}$ *M*, its height decreasing with increasing pH in the form of a dissociation curve. Limiting currents are determined by the rate of formation of the tropylium ion from tropyl alcohol, which is reduced at very negative tensions. The rate constant was calculated according to Koutecký to be $k_2 = 2 \cdot 10^6$ l mol^{-1}sec^{-1}. The rate of formation of tropyl alcohol under equilibrium conditions was calculated to be $k_1 = 5 \cdot 10^{11}$ l mol^{-1} sec^{-1}. Neither the form of the dissociation curve not the pK' values are influenced by the nature of the buffer used, by the presence of pyridinium ions or by the ionic strength. The experimentally verified scheme of the reaction, given in the original paper, presents a new simple type of electrode mechanism. [Ot.So.]

161 – Polarography of pyridine cyclopentadienilide (in Russian). S. I. Zhdanov and L. S. Mirkin (Inst. of Electrochem., University of Moscow, U.S.S.R.). *Collect. Czechoslov. Chem. Communs.*, 26 (1961) 370–379.
The polarographic behaviour of pyridine cyclopentadienilide in neutral and acid ethanolic solutions has been investigated. In neutral solutions, one-electron diffusive anodic wave ($E_{1/2} = +0.01$ V) and a cathodic wave ($E_{1/2} = -1.64$ V) are observed, as well as a kinetic wave ($E_{1/2} \pm -1.3$ V). In acid solutions a cathodic wave ($E_{1/2} = -0.95$ V) is observed, and there is no anodic wave. Reactions, corresponding to the various waves, are proposed. [Ot.So.]

162 – Catalytic evolution of hydrogen ions on the mercury drop electrode by phosphorus hydride

(in German). V. Vojíř (Research Inst. of Organic Syntheses, Pardubice, Czechoslovakia). *Collect. Czechoslov. Chem. Communs.*, 26 (1961) 289–291.
Phosphorus hydride, PH_3, is sometimes present as an impurity in gases, for instance in acetylene, and its determination is important owing to its very toxic properties. The possibility of the polarographic determination of PH_3 in very small concentrations has been studied. A Heyrovskyý-type polarograph V 301 was used with a vessel according to Kalousek, together with a separated saturated calomel electrode. PH_3 was liberated by the hydrolysis of calcium phosphite and was absorbed in water or ethyl alcohol. Acetate buffer pH 5.6 was used as the electrolyte.
PH_3 alone is polarographically inactive and only after addition of small amounts of Pt(IV) salts is a high maximum obtained. The following reactions are proposed:

$$\begin{array}{lll} & PH_4^+ + e & \rightarrow PH_3 + H \\ & PH_3 + H^+ & \rightarrow PH_4^+ \\ \text{summarily,} & H^+ + e & \rightarrow H. \end{array}$$

[Ot.So.]

163 – Determination of equilibrium constants in complex-forming systems on the basis of the investigation of their catalytic polarographic currents (in Russian). K. B. Yatsimirski and L. I. Budarin (Inst. of Chem. Technol., Ivanovo, U.S.S.R.). *Collect. Czechoslov. Chem. Communs.*, 26 (1961) 215–223.
This new procedure for the determination of the equilibrium constants of complex-forming reactions in solutions is based on the investigation of the dependence of the value of the catalytic current on the concentration of the complex compound being formed, using varying amounts of the catalyser. The dependence of the catalytic current on the concentration of phosphoric acid in solutions containing molybdo-phosphoric acid was investigated. [Ot.So.]

164 – Polarographic instant currents. III. *i–t* curves of the diffusion current at high concentrations of amalgam-forming depolarisers (in Russian). J. Kůta and I. Smoler (Polarographic Inst., Academy of Sciences, Prague, Czechoslovakia). *Collect. Czechoslov. Chem. Communs.*, 26 (1961) 224–229.
The instant currents of depolarisers in large concentrations ($5 \cdot 10^{-3}$ *M* and larger) were investigated, using capillaries of 2–50 sec drop-times. As long as there was no electrocrystallisation of the metal from the amalgam on the surface of the mercury drop, the $i-t$ curve obeyed Ilkovič's equation, corrected according to Koutecký. In the case of metals having a tendency to form crystals on the mercury, the shapes of the $i-t$ curves differ from the normal shape. Using capillaries with long drop times, it is possible to investigate the crystals under a microscope, especially in the cases of thallium and silver. [Ot.So.]

165 – pH dependence of the polarographic limiting currents of α-ketoacids (in English). S. Ono, M. Takagi and T. Wasa (Laboratory of Biophysical Chemistry, College of Agriculture, University of Osaka, Japan). *Collect. Czechoslov. Chem. Communs.*, 26 (1961) 141–155.
The pH dependence of the limiting currents of meso-oxalic acid, dihydroxytartaric acid, phenylglyoxylic acid, trimethylpyruvic acid, phenylpyruvic acid, oxalo-acetic acid, pyruvic acid and α-ketoglutaric acid has been investigated. The limiting currents of the first reduction waves of these acids have their maximum values of pH near 4; at pH less than 4 they show appreciable decrease with decreasing pH. The limiting current of some of these acids increases again at pH values less than 1. This characteristic behaviour may be attributed to the dehydration of the carbonyl group, and in some cases also to enolisation. [Ot.So.]

166 – The polarographic determination of the rates of dissociation and recombination of weak acids (in German). H. W. Nürnberg, G. van Riesenbeck and M. von Stackelberg (Institute of Phys. Chem., University of Bonn, Germany). *Collect. Czechoslov. Chem. Communs.*, 26 (1961) 126–139.
The following rates of dissociation were measured: H_3PO_4 (second dissociation, $\log k_1 = 4.41$); H_2SO_3 (second dissociation, $\log k_1 = 3.85$; citric acid (third dissociation, $\log k_1 = 4.65$); veronal ($\log k_1 = 3.65$). The electrolytic vessel was a hydrogen cell previously described by Lingane and Laitinen, with a saturated calomel electrode. The temperature was held constant to 1 or 0.1°. Dipyridyl and *p*-nitraniline were used as catalysers.

167 – Complex salts of formaldoxime (in German). M. Bartušek and A. Okáč (Inst. of Anal. Chem., University of Brno, Czechoslovakia). *Collect zechoslov. Chem. Communs.*, 26 (1961) 52–58.
The polarographic investigation of the complex formation of nickel, manganese and cobalt with formaldoxime has led to the conclusion that in alkaline solutions of pH 13 complexes are formed of the composition: $Ni^{IV}R_6{}^{2-}$, $Mn^{IV}R_6{}^{2-}$, $Co^{III}R_6{}^{3-}$.
It was found that in acid media, buffered by a 0.1 *M* citrate buffer of pH 1.40, formaldoxime forms a long, badly-developed wave of $E_{1/2} = -1.0$ V. This wave shows a maximum at higher concen-

trations even in the presence of 0.01% gelatin. With decreasing acidity the wave is shifted to more negative values and becomes flatter. Such a wave is not formed either by hydroxylamine solutions or by formaldehyde, although it is formed slowly when these are mixed together in the buffer medium. In 0.1 *N* KOH formaldoxime gives an anodic wave at 0.2 V.

168 – Investigation of the rate of equilibrium formation in exchange reactions with strongly acid cation- and strongly alkaline anion-exchangers (in German). J. Vodehnal (Institute for Nuclear Research, Academy of Sciences, Prague, Czechoslovakia). *Collect. Czechoslov. Chem. Communs.*, 26 (1961) 21–36.
The polarographic method described earlier in which the time necessary to obtain the exchange equilibrium of an ion exchanger is determined, has been modified so that it is now possible to investigate the whole course of the reaction. The method has been used to investigate the exchange reactions of hydrogen and zinc ions on one side, and chloride and chromic acid ions on the other. A weighed amount of the ion exchanger is swelled in 0.1 *N* HCl for 48 h, 10 drops of 0.5% gelatin solution being added. The mixture is bubbled with nitrogen for 20 min and the curve of zero intensity registered at a definite rate of agitation. After addition of exactly 2.5 ml of a *ca.* 1 *N* $ZnCl_2$ solution the time curve of the limiting current of the Zn ion reduction was registered at 25° at a branched-off voltage of 1.22 V. When the rate of reaction had decreased, the normal polarographic curves were registered at suitable sensitivities. Similar determinations were carried out with the anion exchanger, using 5 ml of a $9 \cdot 10^{-2}$ *M* K_2CrO_4. [Ot.So.]

169 – Polarographic study of the biuret reaction of cyanuric acid. W. U Malik, A. Aziz Khan and R. Haque (Dept. of Chem., Aligarh Muslim University, India). *Naturwissenschaften*, 48 (1961) 47–48.
In phosphate buffer (pH = 11.0–12.04), which serves also as the supporting electrolyte, the stability constant *K* and its dependence on pH for the biuret complex of cyanuric acid with copper ($2 \cdot 10^{-3}$ *M* $CuSO_4$ + $4 \cdot 10^{-2}$ *M* — $1.6 \cdot 10^{-1}$ *M* cyanuric acid, 0.001% methyl red, phosphate buffer) was evaluated by plotting $E_{1/2}$ against pH. The one-electronic reaction is reversible. *K* is not dependent on the concentration of cyanuric acid but decreases with increasing pH. From the slopes of the straight lines of the plots ($E_{1/2}$–log concentration of cyanuric acid and $E_{1/2}$–pH) it was found that one Cu is combined with one molecule of cyanuric acid and three hydroxyl groups. [H.W.Nür.]

170 – Investigation of the effects of inhibitors in the polarographic reduction of periodate ion (in German). L. Holleck and H. Tuphorn (Institut f. physikal. Chemie, Universität Hamburg, Deutschland). *Naturwissenschaften*, 48 (1961) 71–72.
Adsorbierte Inhibitoren (Campher, Methylcellulose usw.) hemmen besonders irreversible Durchtrittsreaktionen. Perjodat wird in zwei Stufen über Jodat zum Jodid reduziert. Die zweite Stufe wird durch Inhibitoren zu negativeren elektrischen Spannungen verschoben (Campher ist wirksamer als Methylcellulose). Die erste Stufe weist schon in inhibitorfreier alkalischer Lösung ein Minimum auf, und zwar im Spannungsbereich des elektrokapillaren Nullpunktes E_0^σ. Inhibitorzusatz verbreitert dieses Minimum. Wie bei anderen Anionen (zB. $S_2O_8^{2-}$) sind für das Minimum der $H_3IO_6^{2-}$-Reduktion ψ-Effekte verantwortlich, wie sein Ausgleich bei Erhöhung der Leitsalzkonzentration bei negativeren Spannungen als E_0^σ (Kationeneffekt) bzw. seine Vertiefung bei positiveren Spannungen als E_0^σ (Effekt grenzflächenaktiver Leitsalzanionen) beweist. Temperaturerhöhung (50°) bewirkt infolge Reaktionsbeschleunigung Aufhebung der Minima und schwächt die Inhibition durch Beeinträchtigung der Inhibitoradsorption. [H.W.Nür.]

171 – Polarographic determination of mesobilirubine in the presence of bilirubine (in German). B. Tvaroha (I. Medizin. Klinik, Karls-Universität, Prag, Tschechoslowakie). *Naturwissenschaften*, 48 (1961) 99.
Erstmalig wird über eine quantitative Bestimmung (Fehler $< \pm 3\%$) von Mesobilirubin(II) in Gegenwart eines bis zu 20-fachen Bilrubinüberschusses(I) berichtet. In 0.1 *N* NaOH betragen die Halbstufenwerte: I, —1.48 V; II, —1.62 V (S.C.E.). Wegen des flachen Verlaufes der stark irreversiblen Stufen ist die Derivativpolarographie anzuwenden, die konzentrationsproportionale diffusionsbedingte Spitzenströme für Mesobilirubin liefert, während die von Bilirubin nicht ausschliesslich diffusionsbedingt sind. [H.W.Nür.]

172 – Unstable intermediate products in the polarographic, catalytic and photo-sensitized reduction of benzile (in German). H. Berg (Institut f. Mikrobiologie u. experiment. Therapie, DAW, Jena, Deutschland). *Naturwissenschaften*, 48 (1961) 100–101.
Zur polarographischen Identifizierung der Zwischenprodukte der katalytischen (Pd-Wasserstoff) oder Photoreduktion von Benzil dienen dessen Reduktions- und Oxydationsstufen. Durch Einsatz verschiedener polarographischer Arbeitsweisen (cycl. Polarographie am hängenden Hg-Tropfen,

Impulspolarographie mit Dreiecksimpulsen, Kalousek-Umschalter, Wechselspannungspolarographie nach Breyer und oscillographische Polarographie mit konstanter Wechselstromamplitude nach Heyrovský) war eine Identifizierung der Zwischenprodukte und eine quantitative Behandlung der Radikalgleichgewichte sowie die Ermittlung der Tautomerisierungsgeschwindigkeit des Benzils möglich. Das führt zur Aufstellung eines detaillierten Reduktionsmechanismus. [H.W.Nür.]

See also abstracts nos. 13, 14, 53, 58, 69, 74, 75, 183.

4. Potentiometry

173 – Thermodynamic studies of hydrobromic acid in anhydrous ethanol. Loys J. Nunez and M. C. Day (Coates Chemical Laboratories, Louisiana State University, Baton Rouge, La., U.S.A.). *J. Phys. Chem.*, 65 (1961) 164–166.
Electrical tension measurements were made on the cell, Ag |AgBr |HBr(*m*) ethanol |Pt–H_2(1 atm), without a liquid junction at 25°. The standard electrode tension of the silver–silver bromide electrode in anhydrous ethanol was determined to be —0.1939 V on the molar concentration scale and —0.1816 V on the molal concentration scale. Mean molal activity coefficients are tabulated and the a° value for hydrobromic acid in ethanol is determined. A new method for the preparation of silver–silver bromide electrodes is reported. [D.S.Ru.]

174 – Studies on the electrochemistry of carbon and chemically modified carbon surfaces. Bill B. Arnold and George W. Murphy (Dept. of Chem., University of Oklahoma, Norman, Oklahoma, U.S.A.). *J. Phys. Chem.*, 65 (1961) 135–138.
Some factors which influence the behaviour of carbon electrodes in contact with aqueous sodium chloride solutions are analyzed. A concentration cell method for identifying finely divided carbon electrodes as cation- and anion-responsive types has been developed. Commercial graphites investigated were cation-responsive, however anion-responsive types have been prepared. Possible half-cell reactions are discussed for both electrode types and the electrochemical capacities of some electrodes are reported. [D.S.Ru.]

175 – Some thermodynamic properties of the system $PuCl_3$–KCl from electromotive force data. R. Benz (Los Alamos Scientific Laboratory, University of California, Los Alamos, New M.,U.S.A.). *J. Phys. Chem.*, 65 (1961) 81–84.
The molar free energy of formation of plutonium(III) chloride as a function of temperature (650–800°) and of composition in liquid $PuCl_3$–KCl solutions was determined from electrical tension measurements made on reversible galvanic cells of the type $Pu_{(liq)}/PuCl_3-KCl_{(liq)}/Cl_{2(g)}$. The free energy of formation of pure supercooled liquid plutonium(III) chloride at one atmosphere can be represented:

$$\Delta F_1^\circ = —206 + 0.03858T(\text{kcal/mole})(958–1014°\text{K}).$$

The standard free energy of formation of solid plutonium(III) chloride can be represented:

$$\Delta F_1^\circ = —221 + 0.053228T(\text{kcal/mole})(958–1014°\text{K}).$$

[D.S.Ru.]

176 – Dosage des amines par l'acide perchlorique en milieu anhydre. Application de la méthode polarovoltrique. J. E. Dubois et P. C. Lacaze (Faculté des Sciences, Lab. de Chim. org. phys., 1 rue Guy-de-la-Brosse, Paris 5e, France). *Compt. rend.*, 252 (1961) 748–750.
Les Auteurs présentent sous forme de tableaux les résultats de titrages par l'acide perchlorique, des amines suivantes: diéthylaniline; diméthylaniline; monométhylaniline; aniline; butylamine; dibutylamine; triéthylamine; pipéridine; pyridine.
Les solvants utilisés sont l'acide acétique, l'acétonitrile, le méthanol, le nitrobenzène, la méthylisobutylacétone. Le point équivalent du titrage est mis en évidence par potentiométrie à courant non nul. Les auteurs utilisent deux électrodes isométalliques parcourues par un courant faible (non précisé). La netteté du saut de tension au point équivalent varie avec la nature de l'amine titrée et celle du solvant. Dans un grand nombre de cas le dosage est amélioré par l'adjonction d'une très faible quantité de perchlorate de diéthylanilinium (PDA). Les équilibres entre les amines et le PDA sont étudiés par spectrophotométrie. Les Auteurs terminent par une application de l'emploi du PDA au titrage d'un mélange pipéridine–pyridine. [Bad.Lam.]

177 – Formation et préparation des vanadates de cuivre. Contribution à la connaissance des anions polyvanadiques. A. Morette et N. Strupler (Faculté de pharmacie, Paris, France). *Bull. soc. chim. France*, (1961) 154–158.

Les Auteurs estiment incertaine la préparation d'un vanadate de cuivre déterminé. Ils s'efforcent de rendre plus prévisible le résultat de cette opération.

A une solution 0.1 *M* de métavanadate de sodium on mélange, dans des conditions déterminées, une solution 1 *M* de sulfate de cuivre. La mesure de la quantité de cuivre, de vanadium et de sodium contenue dans le précipité (par complexométrie, manganimétrie et spectrophotométrie de flamme), la thermogravimétrie du précipité ,la mesure du pH et de la résistivité des solutions permettent de mettre en évidence deux faits essentiels:

(a) On confirme l'existence d'un décavanadate de cuivre. On montre qu'il s'agit soit d'un mélange de $Na_6(V_{10}O_{28})$ et de $CuNa_4(V_{10}O_{28})$ soit du sel $CuNa_{10}(V_{10}O_{28})_2$. Pour expliquer l'augmentation avec le temps du rapport V/Cu dans la solution, il semble nécessaire de faire intervenir l'hydrolyse de $(V_{10}O_{28})^{6-}$ en $(V_{10}O_{28}H)^{5-}$ et en $(V_{10}O_{28}H_2)^{4-}$.

(b) Il existerait également un pentavanadate de cuivre insoluble dont l'anion aurait pour formule $(V_5O_{16}H_2)^{5-}$. [J.Des.]

178 – The non-aqueous titration of phenolic hydroxyl. E. J. Greehow and J. W. Smith (C.S.I.R.O. Coal Research Station, P.O. Box No. 3, Chatswood, N.S.W., Australia). *Analyst*, 85 (1960) 457–461.

0.1 g of sample was dissolved or suspended in 20 ml pyridine and was titrated potentiometrically with 0.2 *N* sodium aminoethoxide in ethylenediamine, using an antimony indicating electrode and a platinum comparison electrode. An atmosphere of pure nitrogen was employed. The titrant was added in 0.1 ml portions and the sample was stirred until a constant electrical tension was obtained (2–15 min). A single titration took 2 h. With the weakest phenols, *e.g.* hydroquinone and catechol, precipitation of their sodium salts hindered the titration. Addition of an unspecified amount of 2,6-xylenol cured this. Compounds titrable by this method were: hydroquinone, catechol, resorcinol, 1,3- and 1,5-dihydroxynaphthalene, 2-hydroxy-1,4-naphthaquinone, 1,4-, 1:5- and 1,8-dihydroxyanthraquinone, pyrogallol, saligenin. Not titrable were carbozole and indole. [P.O.Ka.]

179 – A volumetric micro determination of organically bound sulphur and organic and inorganic sulphates. R. N. Boos (Merck & Co., Inc., Rahway, N.J., U.S.A.). *Analyst*, 84 (1959) 633–635.

This method is a combination of Schöniger's combustion technique, Fitzgerald's ethylenediaminetetraacetic acid (EDTA) titration and Schmid and Reilley's mercury indicator electrode.

An accurately weighed sample containing not more than 1.5 mg sulphur is placed on a 1 × 1¹/₄ in. strip of Whatman No. 1 filter paper, folded in a strip and fitted with a 1 × ¹/₄ in. wick of filter paper. This is placed in the basket of a Schöniger apparatus. 3 ml of H_2O_2 solution (made by diluting Merck's "Superoxol" five-fold) is placed in the conical flask of the apparatus and the air is displaced by O_2. Ignite the wick, place the basket in the flask and after combustion is complete, shake the flask for 2 min to complete the conversion to sulphate. Transfer contents of flask to a glass evaporating dish, add 10 ml 0.005 *M* $BaCl_2$ and evaporate to dryness to destroy H_2O_2. Stir residue with water, add 2 ml 1 *M* CH_3COONH_4, 0.1 ml of 0.1 *M* mercuric EDTA solution and 2 ml 0.880 NH_3, transfer to 30 ml beaker and titrate potentiometrically with 0.1 *M* EDTA using a mercury indicator and calomel comparison electrode. At the end-point $dE/dV = 3600$. The EDTA was standardised by potentiometric titration with 0.01 *M* Zn^{2+} solution. For water-soluble organic sulphates, direct back-titration was employed without combustion. For inorganic sulphates, other EDTA-chelating cations if present were removed by ion-exchange. An accuracy of *ca.* 2% appeared possible. [P.O.Ka.]

180 – The determination of calcium and magnesium in waters by automatic titration. J. Haslam, D. C. M. Squirrell and I. G. Blackwell (I.C.I. Ltd. Plastics Div., Black Farm Road, Welwyn Garden City, Herts., Great Britain). *Analyst*, 85 (1960) 27–35.

Total hardness was determined by basifying with NH_4OH/NH_4NO_3 buffer, adding a known excess of ethylenediaminetetraacetic acid (EDTA) and potentiometrically back-titrating the excess with standard mercuric nitrate solution using an amalgamated Ag indicator electrode and a saturated calomel electrode fitted with a saturated KNO_3 bridge as comparison electrode. In order to determine Ca^{2+} and Mg^{2+} separately the following method was used. 100 ml of sample + 2 drops phenolphthalein solution was acidified with a 2 ml excess of *N* HCl and boiled 5 min. *N* NaOH was added until pink, then 4 ml excess. Add 0.2 ml 0.004 *M* $Hg(NO_3)_2$ solution and potentiometrically titrate using same electrode as before with 0.02 *M* EDTA. When Ca^{2+} end-point is reached, acidify with *N* HCl adding 1 ml excess, add 10–15 ml *M* NH_4OH continue titration to $Ca^{2+} + Mg^{2+}$ end-point. This method was suitable for using an automatic titrimeter. The EDTA was standardised by potentiometric titration with standard Ca^{2+} solution prepared from AnalaR $CaCO_3$. Accuracy appeared to be ±0.5% for Ca^{2+} and ±1–10% for Mg^{2+} depending on the Ca^{2+}/Mg^{2+} ratio. [P.O.Ka.]

181 – The determination of chlorine by the oxygen flask combustion method. J. Haslam, J. B. Hamilton and D. C. M. Squirrell (I.C.I. Ltd., Plastics Div., Black Farm Road, Welwyn Garden City, Herts., Great Britain). *Analyst,* 85 (1960) 556–560.

The sample containing 5–6 mg Cl is wrapped in filter paper which is fitted with a cotton wool wick and placed in a Pb basket which can be lowered into the O_2-filled 500 ml reaction flask. This flask is fitted with a cylindrical depression 55 × 45 mm in the base. The walls of the flask are thoroughly wetted with 4 ml of $N/4$ NaOH containing 3 drops of 35% $NaHSO_3$ solution. The sample is fired by passing a spark from an H.F. leak tester between a firing electrode and the basket support across the wick, and is then left for 10 min. The walls of the flask are washed into the depression with *ca.* 30 ml of water, 6 drops of 100 vol. H_2O_2 are added to destroy excess $NaHSO_3$ and the solution is slightly acidified with $N/1$ HNO_3. The solution is then titrated *in situ* with $N/100$ $AgNO_3$ using an Ag electrode and automatic titrimeter described previously, deducing the end-point from the maximum slope of the titration curve. Typical results given indicated an accuracy of *ca.* 1%. [P.O.Ka.]

182 – Piles à phases liquides opposant le sodium au potassium. Mme M. Dupeyrat (Lab. de Chim. phys., 11 rue Pierre-Curie, Paris, France). *Compt. rend.,* 252 (1961) 269–270.

L'Auteur réalise des piles du type suivant: Ag |AgCl |KCl (1 *M*) |NaCl (*n M*) | phase organique |KCl (*n M*)| KCl(1 *M*) |AgCl |Ag. Ces piles sont donc constituées par deux demi piles ne différant que par la nature du cation (Na^+ ou K^+) dans un des compartiments; la jonction électrolytique est assurée par une solution d'acide laurique dans le nitrobenzène. On mesure aux bornes de cette pile une tension (pole positif du côté sodium) de l'ordre de 50 mV dans les conditions expérimentales suivantes: $NaCl = KCl = 5 \cdot 10^{-2}$ *M*; acide laurique dans le nitrobenzène $5 \cdot 10^{-3}$ *M*. Lorsque l'acide laurique est remplacé par du bromure de lauryltriméthylammonium, la tension de la pile est nulle. Dans d'autres expériences l'Auteur a remplacé l'acide laurique par des céphalines animales et le nitrobenzène par le butanol. D'une façon générale la tension observée serait due à une différence entre les coefficients de partage des ions Na^+ d'une part et des ions K^+ d'autre part (partage entre la phase aqueuse et la phase organique servant de jonction électrolytique entre les deux demi piles). [Bad.Lam.]

183 – Chemical analysis of calcined molybdenum trioxide. S. Král (S.O.N.P., Kladno, Czechoslovakia). *Hutnické Listy,* 15 (1960) 215–217.

After fusion with Na_2O_2, 2 g of the sample is dissolved in water. Mo is determined in the filtrate as $PbMoO_4$, Cr by titration with $KMnO_4$, V by potentiometric titration with $FeSO_4$ and Al gravimetrically. 5 g of a second sample, dissolved in aqua regia, is used for the determination of Fe by the Zimmermann–Reinhart method and for the determination of Ti colorimetrically with H_2O_2. In the same filtrate Ca is determined as oxalate and Mg as pyrophosphate. The following elements are determined in separate samples using the procedures given: Si gravimetrically; P gravimetrically or volumetrically; Cu and Ni polarographically; Sn polarographically; As volumetrically; Mn by the Proctor–Smith method; sulfide S as H_2S or as SO_2; total S as $BaSO_4$; and C volumetrically after combustion. [Gio.Ser.]

184 – Easy method for the determination of the pCO_2 of the blood. D. Mendel (Institute of Cardiology, London, Great Britain). *Lancet,* (1960) 807.

A detailed description is given of a technique for measuring the CO_2 concentration in blood. The method is based on the use of a syringe electrode, previously described (*Lancet,* (1957) 1125), for the measurement of the blood pH. By some modifications the electrode is adapted for the measurement of pCO_2. [Gio.Ser.]

185 – Potentiometric iodimetric determination of plasmalogen. W. T. Norton (Yeshiva University, New York, U.S.A.). *Biochim. Biophys. Acta,* 38 (1960) 340–342.

A modification of a method described previously, based on the determination of excess iodine with Na_2SO_3 in aqueous solution, is given. The modification consists of determining the end-point potentiometrically instead of visually. Using this modification smaller samples can be analysed with greater accuracy. Coloured samples may be analysed without difficulty. [Gio.Ser.]

186 – Applicability of formol titration to the problem of end-group determination in polynucleotides. D. E. Hoard (Calif. Inst. of Technol., Pasadena, Calif., U.S.A.). *Biochim. Biophys. Acta,* 40 (1960) 62–70.

The reaction of cytidine-5′-phosphate with formaldehyde is studied as a basis for the determination of the chain length in polynucleotides. The reaction is complete in 40 min when 2 *M* formaldehyde is used. Potentiometric titrations under these conditions give results in agreement with those obtained by P analysis. Results are 19% high in the presence of cytidine. The possible reasons for this discrepancy are discussed. [Gio.Ser.]

187 – Rapid determination of minerals and ions in milk. II. Determination of chloride. V. R. Wenner (Nestlé Products, Vevey, Switzerland). *J. Dairy Sci.*, 43 (1960) 22–27.
A volumetric method is described which is suitable for the determination of chloride in milk and milk products. It is based on titration with $Hg(NO_3)_2$ in 1% HNO_3 and is satisfactory for concentrations above 0.1 mg/ml. A rapid and accurate method is based on the measurement of the electrical tension between a silver–silver chloride electrode and a palladium–mercury–calomel comparison electrode, immersed in the solution to be analysed. The chloride can be directly determined with an average error of 2–5% from a calibration graph. Amino acids and other substances which can dissolve AgCl must be eliminated with $CuSO_4$ before the determination. [Gio.Ser.]

188 – Potentiometric determination of manganese in ferro-manganese and other manganese-containing materials (in Czech). A. Jelínek and J. Hošala (Kovohuty Istebné, Czechoslovakia). *Hutnické Listy*, 15 (1960) 137.
Many different manganese-containing materials can be analysed with great accuracy by the method of Lingane and Karplus. A 0.5 g sample is dissolved in 20 ml of HNO_3 and the solution diluted to 500 ml. 100 ml of this solution are treated with 0.5 g of urea and 250 ml of 10% $Na_4P_2O_7$ and the pH adjusted to 6–7. The Mn is titrated potentiometrically with $KMnO_4$, using a platinum electrode and a S.C.E. Co, Cr, Fe, Ni, Cu, Mo, W and U do not interfere, while V does. [Gio.Ser.]

189 – Use of the glass electrode with a sodium function for determining the concentration of sodium ions (in Russian). V. E. Goremȳkin and P. A. Kryukov. *Gidrokhim. Materialy*, 28 (1959) 170–179.
The determination of sodium ions may be carried out with satisfactory accuracy, using a sodium glass electrode, provided the diffusion tension is eliminated. The activity coefficient of sodium ions does not depend on the composition of the solution at ionic strengths less than 0.05, but only on the ionic strength itself. At higher ionic strengths the activity coefficient depends also on the composition of the solution. Equations are given for the calculation of the activity coefficient at ionic strengths greater than 0.1 in solutions of any composition. [Gio.Ser.]

190 – Use of the glass electrode with a sodium function for the analysis of natural waters (in Russian). V. E. Goremȳkin and P. A. Kryukov. *Gidrokhim. Materialy*, 28 (1959) 180–198.
The concentration of Na^+ in natural waters can be easily measured by means of a glass electrode. The method described is very simple and may be used for waters with mineral contents less than 5–6 g/l. The method cannot be used for acidic waters as such, and these must be neutralised before estimation. The $Ca^{2+} + Mg^{2+}$ concentration must not exceed 6 times the Na^+ concentration for correct measurements to be obtained. The error is ±2% in the direct determination, and ±5% in the simplified method. [Gio.Ser.]

191 – Indirect determination of sulfate by non-aqueous titrimetry. G. Goldstein, O. Menis and D. L. Manning (Anal. Chem. Div., Oak Ridge Natl. Lab., Oak Ridge, Tenn., U.S.A.). *Anal. Chem.*, 33 (1961) 266–268.
A method has been developed for the rapid determination of sulfate in the presence of uranyl and ferric ions. An aliquot of the sample, containing from 1–6 mg of sulfate is transferred to a 50 ml beaker. 3 ml of 0.05 *M* barium acetate solution is added together with 6 ml of acetic anhydride for each ml water present and 10 ml acetic acid. The solution is boiled for 2 min and cooled. After this it is diluted to 25 ml with acetic acid and the excess barium acetate is titrated potentiometrically with perchloric acid. The effect of water and anions is studied. The precision of the determination is 1% or better. [Kl.Gr.]

192 – On the accuracy of pH-measurements (in German). K. Slevogt (Institut Entwicklg. chem. phys. Analysenmeth., Weilheim/Obb., Deutschland). *Mitt. Inst. Entwicklg. chem. phys. Analysenmeth.*, 4 (1960) 90–95.
Die Betrachtungen beziehen sich unter Weglassen aller theoretischer Zusammenhänge auf die durch die Messkette und das Messgerät (beide zusammen als "pH-Meter" aufgefasst) verursachten Fehler. Neben einer kurzen Darstellung der "Elektrodenfehler" wird besonders auf die Forderungen eingegangen, welche an ein Röhrenvoltmeter hinsichtlich der Eignung als pH-Meter zu stellen sind. [Fr.Oe.]

193 – An interpretation of the end-point error in the potentiometric titration of bromide and chlo-

ride mixtures with silver nitrate. R. C. Bowers, L. Hsu and J. A. Goldman (Dept. of Chem., Northwestern University, Evanston, Ill., U.S.A.). *Anal. Chem.*, 33 (1961) 190–194.
Factors influencing the bromide end-point error in the titration of bromide and chloride mixtures have been investigated. The error is reduced to a minimum by adding sufficient electrolyte to cause flocculation of the silver bromide formed. With equimolar amounts of bromide and chloride this minimum error is between 1.2 and 1.5%. Under non-flocculation conditions the end-point error is dependent upon the rate of addition of silver nitrate and the ratio of bromide to chloride. Upon flocculation of the chloride-rich colloid, rapid exchange occurs and distribution of the chloride and bromide between solid and solution is nearly that expected for ideal homogeneous mixed crystals. [Kl.Gr.]

194 – The reaction of chromates with diphenyl-carbazide (in English). J. Minczewski and W Żmijewska (Dept. of Anal. Chem., Institute of Nuclear Research, Polish Academy of Science, Warsaw, Poland). *Roczniki Chem.*, 34 (1960) 1559–1570.
The reactions of Cr(VI) with diphenyl-carbazide (DPCD) and Cr(II) with diphenyl-carbazone (DPCN) were investigated spectrophotometrically and by potentiometric titration. On the basis of the method of continuous variation and spectrophotometric and potentiometric titration the ratio of the components was established. The reaction is composed of at least two steps, namely a redox reaction involving the DPCD–DPCN couple, and the formation of a coloured product with the probable formula DPCN.Cr(III). Various decoloration reactions were also explained. Additional experiments were performed by extraction of the coloured compound and investigation of the behaviour of DPCN in organic acids. In the latter case the chromophore system was stabilised by a proton. The lack of reaction between Cr^{3+} ion and DPCN was explained on the basis of strong hydration of the Cr^{3+} ion, which inhibits direct reaction. [Ad.Hu.]

195 – Potentiometric titration of copper with sodium diethyldithiocarbamate (in English). A. Hulanicki (Dept. of Inorg. Chem., University of Warsaw, Poland). *Chemia anal.*, 5 (1960) 881–887.
An analytical method for the determination of milligram amounts of copper in the presence of a 25-fold excess of ferric ions has been developed. It involves the potentiometric titration of copper with sodium diethyldithiocarbamate using a silver indicator electrode. This electrode should be properly prepared before titration by soaking it in the titrant solution. Best results were obtained in a 0.2 *M* ammonia buffer solution of pH about 9.0. The excess of ferric iron should be complexed by means of nitric acid, but ferrous iron should be initially oxidised by means of nitric acid. Aluminium, among other ions, does not interfere, but silver, nickel, cobalt and mercury must be absent. Lead, cadmium and zinc do not interfere seriously if, during the course of the titration, the carbamate formed is extracted with diethyl ether. The average coefficient of variation is about 0.5%. This procedure was used for the determination of the total copper during the analysis of cuprous chloride. [Ad.Hu.]

196 – Unusual proton affinities of some mixed ligand iron(II) complexes. Alfred A. Schilt (Dept. of Chem., University of Michigan, Ann Arbor, Mich., U.S.A.). *J. Am. Chem. Soc.*, 82 (1960) 5779–5783.
The protonation of the neutral dicyano-bis-(1,10-phenanthroline)–iron(II) and dicyano-bis-(2,2′-bipyridine)–iron(II) complexes has been examined in acetic acid and chloroform solvents. Potentiometric titration with perchloric acid gives an electrical tension break at a mole ratio of 1 : 1, indicating monoprotonation of the complexes. The monoprotonated form tends to precipitate. The variation of the spectra of the complexes for a series of mole ratios of $HClO_4$–complex indicates that diprotonation occurs at high mole ratios. Exchange constants using thiourea and *o*-chloroaniline as reference bases were measured in acetic acid. The basic strength of the complexes is comparable to that of the reference bases. A tentative rationalization of this unusual case of protonation is given. [Roy.Mur.]

197 – Equilibrium electrical tensions of metals in molten electrolytes (in Russian). M. V. Smirnov and L. D. Yushina. *Izvest. Akad. Nauk S.S.S.R., Otdel Khim. Nauk*, (1959) 251–258; *Nuclear Sci. Abstr.*, 13 (1959) abstr. No. 9743. [Ed.]

198 – Potentiometric differential titration of organic bases in methylethylketone medium (in Russian). A. P. Kreshkov, L. N. Bykova and N. S. Shemet. *Doklady Akad. Nauk S.S.S.R.*, 134 (1960) 96–99.
The Authors have tried to titrate various organic bases (primary, secondary, teriary and quaternary amines, aliphatic and aromatic) and mixtures of these. Various solvents were investigated. The best was found to be methyethylketone. Titrations were carried out using a solution of $HClO_4$ in methylethylketone. A glass–calomel electrode pair was employed. It was found that mixtures of tetraethylammonium hydroxide, triethylamine, pyridine and *m*-toluylenediamine may be determined with an error of 2%. [Ot.So.]

199 – Chelates. II. Piperazine-carbonic and dicarbonic acids (in Italian). A. Rescigno and D. Pitrè (Bracco Industria Chimica, Milan, Italy). *Ann. chim.* (*Rome*), 51 (1961) 151–157.
Dissociation constants were determined potentiometrically with a glass electrode in 0.1 *M* KCl at 22° for the following acids:

	$\log K_{H_3Z}$	$\log K_{H_2Z}$	$\log K_{HZ}$
Piperazine-monocarbonic	1.6	5.41	9.53
Piperazine-2,3-dicarbonic	—	5.44	10.25
Piperazine-2,5-dicarbonic	—	5.56	9.05
Piperazine-2,6-dicarbonic	—	5.42	9.08

Chelate formation occurs between these acids and Mg^{2+}, Ca^{2+}, Sr^{2+}, Co^{2+}, Cu^{2+}, Ag^{+}, Zn^{2+}, Cd^{2+}, Hg^{2+} and Pb^{2+}. [Fr. Pan.]

200 – Potentiometric titration of alkali ferrocyanide with bismuth nitrate solution (in Polish). Z. Orylski (Dept. of Inorg. Chem., Copernicus University, Toruń, Poland). *Chemia anal.*, 5 (1960) 917–921.
It was found that the composition of the precipitated bismuth ferrocyanide depends upon the alkali metal of the titrate. In the case of potassium salt titrated with $Bi(NO_3)_3$ the precipitate composition was $4Bi_4[Fe(CN)_6]_3 \cdot 3K_4Fe(CN)_6$, and an error of +2% was found to occur compared to the gravimetric determination. In the case of lithium or sodium salts the precipitate with the composition $Bi_4(Fe(CN)_6)_3$ or $5Bi_4(Fe(CN)_6)_3 \cdot 2Bi(NO_3)_3$ was obtained. In general two end-point breaks were obtained, the second being the more distinct. In dilute solutions one break corresponding to $Bi_4(Fe(CN)_6)_3$ was obtained, and in concentrated solutions one break corresponding to the mixed salt formation was found. The accuracy compared to gravimetric methods was quite good, but in the vicinity of the equivalence-point the electrical tensions were established very slowly. [Ad.Hu.]

201 – Argentometric determination of 2-mercaptobenzothiazole in technical and crude products (in Polish). W. Czerwiński and H. Vieweger (Struszyński Anal. Dept., Inst. of Gen. Chem., Warsaw, Poland). *Chemia anal.*, 5 (1960) 1011–1019.
An argentometric method for 2-mercaptobenzothiazole determination has been modified and applied to the analysis of crude products. It consists of potentiometric titration with a silver chloride–glass electrode pair using an acetone solution of the sample. As titrants alcoholic solutions of 0.1 *N* $AgNO_3$ and 0.1 *N* NH_3 were used. These solutions were added alternately from two burets, starting with the $AgNO_3$ solution. This procedure eliminated the interference of thiocarbanilide which may be present as a contaminant. The end-point was found from the titration curve. In the absence of thiocarbanilide, as in the analysis of technical 2-mercapto-benzothiazole, $AgNO_3$ alone was used as the titrant. In this case silver chloride and mercury sulphate electrodes were used. Any other impurity present in the samples does not interfere in these determinations. [Ad.Hu.]

202 – Application of the potentiometric method to detection of some substances on paper chromatograms (in Polish). A. Gołebiowska (Dept. of Gen. Chem., Jagiellonian University, Kraków, Poland). *Chemia anal.*, 5 (1960) 1021–1026.
A potentiometric method was applied to the detection on paper chromatogram zones of some physiologically active substances such as dionine, eukodal, quinine and cinchonine in the form of free bases or their HCl salts. The chromatograms were developed by the ascending method on Whatman No. 1 filter paper. *n*-Butanol–water was used as the solvent with addition of NH_4OH and glacial CH_3COOH for free bases and their salts, respectively. The positions of the substances were detected with the microcell, Sb |0.1 *N* KCl |investigated solution |Sb, connected to a Wulff electrometer. The chromatograms moistened with 0.01 *N* HCl or with distilled water were tested with a microcell every 3 mm along the longitudinal axis of the paper strip. The R_f values were measured and compared to those obtained by the chemical method. Binary and ternary mixtures of the substances mentioned were separated, and the concentrations were given when the separation was effective. [Ad.Hu.]

203 – Indicator properties of guaiacolphthalein (in Polish). J. Gronowska (Dept. of Org. Chem., Copernicus University, Toruń, Poland). *Roczniki chem.*, 34 (1960) 1799–1805.
The indicator properties of guaiacolphthalein have been studied. In acidic solutions it was colourless, in alkaline — violet. Solutions of guaiacolphthalein were titrated potentiometrically in 20% ethanol. It was found that the colour change takes place over the pH range 8.4–10.2. In strongly alkaline solutions (pH > 14) the indicator was decolorised. In conc. H_2SO_4 a red solution was obtained which was reversibly decolorised upon dilution with water. The p*K* value of guaiacolphthalein was found by a colorimetric method to be equal to 9.7. These results indicate that guaiacolphthalein is a suitable alkalimetric indicator. [Ad.Hu.]

204 – The third ionization constant of 1,2-naphthaquinone-1-monoxime-3,6-disulphonic acid (in English). Osmo Mäkitie (Dept. of Soil Science, Agricultural Research Centre, Helsinki, Finland). *Suomen Kemistilehti*, 33 (1960) B 207–209.
The value, 7.51, has been obtained potentiometrically at 25° for the third thermodynamic ionization constant (pK_3°) of 1,2-naphthaquinone-1-monoxime-3,6-disulphonic acid in water.
[Sta.Bred.]

205 – Potentiometric determination of the solubility product of silver(I) oxide in potassium nitrate and sodium perchlorate solutions (in English). Reino Näsänen and Paavo Meriläinen (Dept. of Chem., University of Helsinki, Finland). *Suomen Kemistilehti*, 33 (1960) B 197–199.
The equilibrium between silver(I) oxide and an aqueous solution of silver nitrate with which it is in contact has been investigated by a simple pH method. Extrapolation to zero ionic strength gave the value $\log K_s^\circ = -7.71$ for the equilibrium constant of the reaction: $\frac{1}{2}\ Ag_2O + \frac{1}{2}\ H_2O \rightleftharpoons Ag^+ + OH^-$.
The solubility product of silver(I) oxide in potassium nitrate and sodium perchlorate solutions was also determined. [Sta.Bred.]

206 – Further studies on the formation of catechol-3,5-disulphonic acid complexes of some divalent metals (in English). Reino Näsänen (Dept. of Chem., University of Helsinki, Finland). *Suomen Kemistilehti*, 33 (1960) B 111–114.
The formation of complexes between catechol-disulphonic acid (L) and divalent cobalt, nickel, zinc, cadmium and lead has been investigated in molar aqueous sodium perchlorate solution. The equilibria involved proved to be more complicated than in earlier studies of the Author in which no neutral salts were added to the medium because of the overlapping of several reactions. On the other hand, the stabilities of the complexes ML_2^{6-} could be determined which is more difficult when no neutral salt has been added. The potentiometric titration method using a glass electrode for the determination of the hydrogen ion concentration was employed. The stability constants of the complexes ML^{2-} and ML_2^{6-} for the above metals were determined. The formation of complexes of the type MHL^- could not generally be confirmed although a slight contribution was expected on the basis of the results of the previous studies without addition of neutral salts.
[Sta.Bred.]

207 – On chelate formation by pentaerythritol with oxyacids (in English). P. J. Antikainen and V. M. K. Rossi (Inst. of Chem., University of Helsinki, Finland). *Suomen Kemistilehti*, 33 (1960) B 94–97.
The ability of pentaerythritol to form chelates with arsenious, boric, germanic and telluric acids in aqueous solutions has been studied potentiometrically. It appears that pentaerythritol forms weak 1 : 1 or 1 : 2 (acid : ligand) anionic chelates with all the above-mentioned acids except germanic acid, with which it does not seem to form a chelate. The respective chelation constants have been determined and the results are compared with the results of earlier studies of the chelation of polyols and oxyacids. [Sta.Bred.]

208 – The ionization, chelate formation and ultraviolet absorption of 2-furoic, 2-pyrrolecarboxylic and 2-thiophenecarboxylic acids in aqueous salt solutions (in English). Paavo Lumme (Lab. of Propaedeutic Chemistry, University of Helsinki, Finland). *Suomen Kemistilehti*, 33 (1960) B 87–93.
The ionization of 2-furoic acid, 2-thiophenecarboxylic acid and 2-pyrrolecarboxylic acid in aqueous potassium chloride solutions has been studied potentiometrically. The thermodynamic ionization constants and the changes in the free energy, enthalpy and entropy of the ionization processes have been evaluated. The ionization reactions are exothermic. The ultraviolet spectra of 2-furoic and 2-thiophenecarboxylic acids were recorded and the stability constants of their first copper(II) and calcium complexes determined. The results are discussed. [Sta.Bred.]

209 – Solubility products of some divalent metal anthranilates in water (in English). Paavo Lumme (Lab. of Propaedeutic Chemistry, University of Helsinki, Finland). *Suomen Kemistilehti*, 33 (1960) B 69.
The solubility products of divalent copper, cobalt, nickel, zinc, cadmium and lead anthranilates have been determined potentiometrically in water at 25°. The solubility order is the same as found previously for many other divalent metal carboxylates. [Sta.Bred.]

210 – Chelation of germanic acid with some *o*-diphenols in aqueous solution (in English). P. J. Antikainen and P. J. Mälkönen (Inst. of Chem., University of Helsinki, Finland). *Suomen Kemistilehti*, 32 (1959) B 179–182.
The potentiometric titration of germanic acid in the presence of some *o*-diphenols (catechol, pyrogallol and the disodium salt of catecholdisulfonic acid, Tiron) reveals the formation of dibasic

chelate acids in which three phenol molecules are bound by one germanic atom. The corresponding chelate formation constants have been determined. [Sta. Bred.]

211 – Potentiometric and spectrophotometric studies on the ionization of violuric, barbituric and 5,5-diethylbarbituric acids (in English). Reino Näsänen and Tapio Heikkilä (Dept. of Chem., University of Helsinki, Finland). *Suomen Kemistilehti*, 32 (1959) B 163–170.
The first and second acid dissociation constants of violuric, barbituric and 5,5-diethylbarbituric acids have been determined by the pH method. The values $pK_1^\circ = 4.58$ and $pK_2^\circ = 10.06$ (25°, $I = 0$) were obtained for violuric acid, the values $pK_1^\circ = 4.08$ and $pK_2^\circ = 12.28$ for barbituric acid and the values $pK_1^\circ = 8.00$ and $pK_2^\circ = 12.8$ for 5,5-diethylbarbituric acid. The effect of potassium chloride additions on the acid dissociation constants was also investigated. In addition, the second acid dissociation constant of diethylbarbituric acid was determined spectrophotometrically. The ultraviolet absorption spectra of the three species of acids have been determined and are discussed. The spectra of the uni- and di-negative ions of violuric acid in the visible range were also determined. [Sta. Bred.]

212 – The determination of the acidity constants of highly ionized simple ampholytes. The first ionization constants of 2-pyridinecarboxylic and 8-quinolinecarboxylic acids (in English). Paavo Lumme (Lab. of Propaedeutic Chemistry, University of Helsinki, Finland). *Suomen Kemistilehti*, 32 (1959) B 153–156.
It has been found possible to determine the acidity constants of highly ionized simple ampholytes in aqueous solution with a relatively high accuracy by measuring the electrical tension of the cell: glass electrode|RH, HCl, KCl| AgCl, Ag. The basic condition is a sufficiently high solubility of the ampholyte. The values 0.79 and 1.82 were obtained for the first thermodynamic ionization constant $pK_{1,0}$ of 2-pyridinecarboxylic and 8-quinolinecarboxylic acids respectively at 25°. [Sta. Bred.]

213 – Potentiometric studies on histamine and its metal chelates. II. The cadmium and nickel chelates of histamine in aqueous solutions (in English). S. N. Randolf von Schalien (Dept. of Chem., Finland Institute of Technology, Helsinki, Finland). *Suomen Kemistilehti*, 32 (1959) B 148–153.
The ionization of histamine and the stabilities of the 1 : 1 cadmium and nickel chelates of histamine in dilute salt solutions have been potentiometrically investigated over the temperature range 25°–50°. The thermodynamic ionization constants were determined at 37° and 50° and the thermodynamic stability constants of the 1 : 1 cadmium and nickel chelates at 25°, 37° and 56°. Using these constants and the previously determined ionization constants of histamine at 25°, the entropy and enthalpy changes in the ionization, and the formation of the 1 : 1 cadmium and nickel chelates were calculated. The ratio $\Delta H^\circ/pK_0$ for the imidazole ionization of histamine has been found to be approximately equal to that for the NH_2 ionization. [Sta. Bred.]

214 – Potentiometric studies on histamine and its metal chelates. III. The copper chelate of histamine in aqueous solution (in English). S. N. Randolf von Schalien (Dept. of Chem., Finland Institute of Technology, Helsinki, Finland). *Suomen Kemistilehti*, 33 (1960) B 5.
The thermodynamic stability constant of the 1 : 1 copper chelate of histamine has been potentiometrically determined at 25°, 37° and 50°. The standard molar heats and entropies have been calculated. The ratios $\Delta H^\circ/pK_0$ for the two stages of ionization of histamine and the ratio $\Delta H^\circ/\log k_{1,0}$ for the formation of the 1 : 1 cadmium, nickel and copper chelates of histamine have all been found to be approximately equal. [Sta. Bred.]

215 – The thermodynamics of anionic chelate formation. II. The effect of temperature on the chelation of boric acid and catechol (in English). P. J. Antikainen and Asko Kauppila (Inst. of Chem., University of Helsinki, Finland). *Suomen Kemistilehti*, 32 (1959) B 141–144.
It was found by a potentiometric method that two different chelate acids (1 : 1 and 1 : 2) exist in solutions of boric acid and catechol. The stoichiometry and formation constants of these reactions have been determined at different temperatures and the thermodynamic quantities ΔH, ΔG° and ΔS° have been computed as functions of temperature. Both chelation reactions seem to be exothermic in the standard state, but the corresponding enthalpy changes are very small ($\Delta H = 48$–68 cal/mole). The entropy changes for the reactions are positive and vary between 16–21 E.U. The free-energy changes for both reactions are independent of temperature. These thermodynamic values indicate that the entropy effect mainly contributes to the free-energy change. [Sta. Bred.]

216 – Precise measurements, with the glass electrode, of the ionisation constants of benzoic, phenylacetic and β-phenylpropionic acids at 25°. Edward J. King and J. E. Prue (Reading University, Great Britain). *J. Chem. Soc.*, (1961) 275–279.

In order to eliminate electrochemical reduction of the acids, the hydrogen electrode has been replaced by a low resistance glass electrode, giving a precision of better than 0.1 mV (or 0.002 pH) in the tension.
A cell without liquid junction is used, by means of a comparison silver–silver chloride electrode. The asymmetry tension effect is avoided by measuring the change of tension at the moment of transfer of the glass electrode from a cell containing a buffer solution of acetic acid to the cell containing the solution under study.
The thermodynamic p*K* values at 25° are: 4.2050 ± 0.0015 (benzoic acid); 4.3074 ± 0.0010 (phenylacetic acid); and 4.6644 ± 0.00055 (β-phenylpropionic acid). [L.Gi.]

217 – Hydrazine sulphate as a volumetric reagent (hydrazinometry). VII. Determination of mercury-(II) (in German). J. Vulterin (Economics Faculty, Institute of Chemical Industry, Technical University, Prague, Czechoslovakia). *Collect. Czechoslov. Chem. Communs.*, 26 (1961) 317–320.
Conditions have been determined for the direct potentiometric determination of Hg(II) using hydrazine sulphate volumetric solution as the reducing reagent. Solid KI or KBr is added to the solution containing about 10–300 mg Hg(II) until the precipitate formed becomes nearly redissolved (0.5–1 g). The mixture is diluted with water and KOH is added to bring its final concentration to about 0.75–5% in the case of bromide and 23–33% in the case of iodide. The solution is then titrated with a 0.1 *N* or 0.1 *M* hydrazine sulphate solution, indication of the end-point being potentiometric with a platinum and a saturated calomel electrode. The directive coefficient of the tension change at the equivalence-point is about 10000, the inflexion point occurring at 320 mV (S.C.E.). Tension stabilisation is practically immediate. The method may be used in the presence of NO_3^-, SO_4^{2-}, CO_3^{2-}, F^-, Cl^- and Br^-, its mean relative deviation being 0.35%.
[Ot.So.]

218 – Stability of the chelates of benzene-tricarboxylic acids formed with bivalent metals. M. Yasuda (Chemical Inst., Faculty of Science, Nagoya University, Japan). *Z. physik. Chem. (Frankfurt)*, 27 (1961) 333–342.
The stability constants of the chelates of hemimellitic and trimellitic acid with Cu and Ni were determined in aqueous solution at 25° by potentiometric titration, measuring the pH with a glass electrode combined with an electronic amplifier. The stabilities of hemimellitic acid chelates are larger than those of trimellitic acid chelates and comparable with those of phthalic acid chelates and their derivatives. [H.W.Nür.]

219 – Ionization of hydrazides of *o*-, *m*- and *p*-aminobenzoic acids. V. D. Canić (Institute of Chem., Faculty of Medicine, Beograd, Jugoslavia). *Naturwissenschaften*, 46 (1959) 575–576.
The ionization constants were determined potentiometrically at 25°. The higher p*K*-value probably belongs to the NH_2-group and the lower p*K* to the hydrazine nitrogen. The properties are compared with those of pyridine carboxylic acids and with those of the esters of both groups of acids.
[H.W.Nür.]

220 – The determination of activity coefficients of hydrochloric acid and *p*-toluenesulfonic acid in mixed aqueous solutions from electromotive force measurements. O. D. Bonner and Linda Lou Smith (Dept. of Chem., University of South Carolina, Columbia, S.C., U.S.A.). *J. Phys. Chem.*, 64 (1960) 261–266.
Electrical tension measurements of the cells Pt, $H_2/HCl(m_1)$, *p*-TSA $(m_2)/AgCl(s)$, Ag were used to determine the acitivity coefficients of hydrochloric acid and *p*-toluenesulfonic acid at 25° in binary aqueous solutions. At constant molality the activity coefficients of HCl are decreased by the addition of *p*-toluenesulfonic acid, while the coefficients of *p*-toluenesulfonic acid are increased by the addition of HCl. Harned's rule is obeyed in moderately concentrated solutions. [D.S.Ru]

221 – Kinetics of the cathodic reduction of anions: germanium oxides. Mino Green and P. H. Robinson (Lincoln Laboratory, Massachusetts Inst. Technol., Lexington, Mass., U.S.A.). *J. Electrochem., Soc.*, 106 (1959) 253–260.
The cathodic reduction of GeO_3^{2-} anions in the electrochemical cell Hg(Na) |GeO_2, NaOH(aq) |Pt gives GeH_4, Ge and H_2 as end products at the cathode. The current efficiency for GeH_4-formation is > 40% and the mass conversion efficiency > 80%. The partial current of GeH_4, Ge and H_2 formation has also been measured. A highly reducing intermediate product with a mean life of ~4 min has been detected in solution but its nature has not been established. The value for the Tafel-slope of GeH_4-formation is given as —56 ± 2 mV per decade of current density. The mechanism for the overall reaction:

$$GeO_3^{2-} + 7\ H_2O + 8\ e^- \rightarrow GeH_4 + 10\ OH^-$$

is discussed.
Further experiments for the determination of the rate-determining step are suggested. [Fe.Jol.]

222 – The instability constants of the complexes of divalent platinum. A. A. Grindberg, G. A. Shagisultanova and M. I. Gelfman (Technol. Inst. of Lensoviet, and Radium Inst., Academy of Sciences, Leningrad, U.S.S.R.). *Svensk Kem. Tidskr.*, 73 (1961) 18–24.

Recent investigations in Leningrad of the equilibria of platinum(II) complexes are reviewed. It has been possible to determine the equilibrium constants using a reversible Pt^{2+}/Pt electrode. The authors measured the total constant B_4^- for a dissociation of the type: $Pt\ X_4^{2-} \rightleftharpoons Pt^{2+} + 4\ X^-$. They also measured the tension of cells of the type: Pt/K_2PtX_4, $KX//KCl_{sat.}$, Hg_2Cl_2/Hg. The measurements were carried out at 18° using slightly platinized platinum electrodes. The ionic strength was adjusted to 1.0 by the addition of $NaNO_3$.

Total constants B_4^- of the ion PtX_4^{2-}:

ion	*log B₄*	B_4^{-1}
$PtCl_4^{2-}$	16.6	$2.5 \cdot 10^{-17}$
$PtBr_4^{2-}$	20.4	$4.0 \cdot 10^{-21}$
PtI_4^{2-}	29.6	$2.5 \cdot 10^{-30}$
$Pt(CN)_4^{2-}$	41.0	$1.0 \cdot 10^{-41}$

[Sv.Li.]

223 – The third acid dissociation constant of 5-sulphosalic acid (in English). Reino Näsänen and Kristina Pakkola (Dept. of Chem., University of Helsinki, Finland). *Suomen Kemistilehti*, 34 (1961) B 19–23.

The third acid dissociation constant of 5-sulphosalic acid has been determined spectrophotometrically and potentiometrically at 25°. The effect of sodium perchlorate on the dissociation was also studied. The values of the third acid dissociation constant at the ionic strengths 0, 0.1, 1, 2 and 3 were found to be $10^{-12.53}$, $10^{-11.87}$, $10^{-11.47}$, $10^{-11.53}$ and $10^{-11.69}$ respectively. The potentiometric and spectrophotometric results were in fair agreement. An equation of the Debye–Hückel type is given for the calculation of the constant at a given ionic strength. The significance of the value of the third acid dissociation constant in the calculation of the stability constants of metal complexes of sulphosalicylic acid is discussed and recalculated. Values for copper complexes are given. [Sv.Li.]

224 – The reaction of iodoacetate and iodoacetamide with proteins as determined with a silver/silver iodide electrode. D. C. Watts, B. R. Rabin and E. M. Crook (Dept. of Biochemistry, University College, London, Gt. Britain). *Biochim. Biophys. Acta*, 48 (1961) 380–388.

The procedure for the preparation of a silver/silver iodide electrode is described. The electrode behaves reversibly, and the tension is linear from 10^{-3}–10^{-6} *M* iodide concentration. A ten-fold change in iodide concentration causes a change of 60 mV in the e.m.f. of the cell at 25°. Reproducibility is to within ±0.05 mV. The electrode described is particularly suitable for following the reaction of iodo-compounds with low concentrations of thiols, by measuring the iodide produced. Applications to the determination of SH groups in proteins and other thiol compounds are shown. The presence of two reactive SH groups in the enzyme, creatine phosphokinase, has been demonstrated. The results on native and denatured egg-albumin are not conclusive. [Gio.Ser.]

225 – Complexes of ethylene-bis-thioacetic acid with bivalent cations (in Italian). G. Saini, G. Ostacoli, E. Campi and N. Cibrario (Inst. of Anal. Chem., Turin University, Italy). *Gazz. chim. ital.*, 91 (1961) 242–259.

In aqueous solution, at 20° and ionic strength 0.1, the formation of 1 : 1 complexes occurs between $(CH_2)_2(SCH_2COOH)_2$ (denoted more simply as H_2A) and Cu^{2+}, Cd^{2+}, Zn^{2+} and Ca^{2+}; the species MeA and $MeHA^+$ are both present. The dissociation constants of H_2A are: $pk_1 = 3.39$; $pk_2 = 4.21$. The logarithms of the stability constants, as determined potentiometrically, are: $k_{CuA} = 5.66$; $k_{CuHA} = 3.98$; $k_{CdA} = 2.85$; $k_{CdHA} = 1.93$; $k_{ZnA} = 2.61$; $k_{ZnHA} = 1.74$; $k_{CaA} = 1.74$; $k_{CaHA} = 1.16$. [Fr.Pan.]

226 – Nullpoint potentiometric determination of fluoride. T. A. O'Donnell and D. F. Stewart (Dept. of Chem., University of Melbourne, Victoria, Australia). *Anal. Chem.*, 33 (1961) 337.

The method described is based on the formation of a complex of Ce(IV) with fluoride. This decreases the redox tension of the Ce(IV)–Ce(III) couple. The unknown fluoride is added to a Ce(IV)–Ce(III) half-cell and the potential difference of another half-cell of the same type but without fluoride is used as a reference. A standard fluoride solution is added to the comparison half-cell until the potential difference between the cell and the test solution is zero. The application of the method to the determination of fluoride in binary and complex coumponds, in William Winter distillates, in eluates from ion exchange columns, and in pyrolysis distillates is described. Chloride, nitrate, and sulfate do not interfere. The mean percentage deviation is below 0.2%.

[Kl.Gr.]

227 – Potentiometric determination of chlorine bound to boron in mixtures containing 2-chlorovinyl boron chlorides and ethyl boron chlorides. H. G. Nadeau, D. M. Oaks and R. D. Buxton (Mathieson Chem. Corp., New Haven, Conn., U.S.A.). *Anal. Chem.*, 33 (1961) 341.
The paper describes the determination of chloride in highly air-sensitive substances, such as dichloro-2-chlorovinylborane, chlorodiethylborane, boron trichloride and others. The preparation of the sample is carried out in a dry box. After weighing approximately 0.4 ml of the sample into a gelatine capsule in a dry box and dosing the capsule, it is placed in an Erlenmeyer flask, which has been filled with nitrogen and containes 60 ml of a 1 : 2 concentrated nitric acid–methanol solution. The flask is stoppered and left to stand for 10 min. After transferring the solution to a 400 ml beaker, using methanol as a wash, the hydrochloric acid present is titrated with standard silver nitrate, using a glass and a silver–silver chloride electrode. [Kl.Gr.]

228 – Ionization constants for some piperazine derivatives. Donal A. Keyworth. *J. Org. Chem.*, 24 (1959) 1355–1356.
Potentiometric titration with a glass electrode is performed on a 0.0005 *M* solution of the appropriate amine, the titrant being 0.5 *N* HCl.

From the titration curve and by using the activity coefficients of OH^- (Kortüm and Bockris) the classical p*K* values for 9 pyperazine derivatives have been calculated. Substitution always causes a decrease in basicity, the effect being greater in the 1,4-position. The results are summarized in a table, in which the ionic strength at which the p*K* was calculated is specified. [Ca.Cas.]

229 – Basicity and ionization constants of some pyrazine derivates. Donal A. Keyworth. *J. Org. Chem.*, 24 (1959) 1355.
With the aid of spectrophotometric and electrometric techniques, ionization constants are evaluated on the basis of the relative concentrations of the free and monoprotonated base, calculated from spectrophotometric measurements (it is assumed that in 1 *M* HCl the base is monoprotonated and that in 0.1 *N* NaOH it is completely non-protonated), $[OH^-]$ being calculated from pH, ionic strength and activity coefficients (Kortüm and Bockris). The basicity increases with methyl-substitution, the effect being larger when substitution occurs on two C atoms adjacent to the same N atom. [Ca.Cas.]

230 – Complex formation between copper and some organic acids, phenols and phenolic acids occurring in fruit. C. F. Timberlake (Long Aston Research Station, Bristol University, Gt. Britain). *J. Chem. Soc.*, (1959) 2795–2798.
Potentiometric studies have shown that copper can combine with the *o*-diphenolic groups of (+)-catechin, chlorogenic acid and caffeic acid in a manner similar to its reaction with catechol. Data were obtained by carrying out potentiometric titration of these compounds with alkali, with and without the presence of cupric chloride. It was shown that in solutions of pH less than 4 cupric ions combine with the carboxyl group of chlorogenic acid. The stability constants of the copper complexes are rpesented and the stabilities of those with chlorogenic and quinic acids are compared with that with dehydroshikimic acid. [G.F.Rey.]

231 – Complex compounds of cerium, neodymium and samarium with gluconic acid (in Russian). N. A. Kostromina. *Zhur. Neorg. Khim.*, 5 (1960) 95–101.
Measurement of conductance, potentiometric titrations and determinations of the ionic transport were applied in studying the formation of complexes in systems consisting of cerium, neodymium and samarium chlorides and gluconic acid. All the elements of the cerium group (Ce, Nd, Sm) were found to form complexes containing from one to six gluconate radicals, analogous to those formed by lanthanum. In correlation with the increasing stability of the complexes of this series, it was noted that they are formed at pH values which decrease from lanthanum to samarium. The author isolated and analysed in detail the complexes of neodymium chloride with gluconic acid, studied some of their properties and proposed formulas for them. [Li.Ne.Ro.]

232 – Redox potentials of plutonium in acid solutions of different ionic strength (in Russian). O. L. Kabanova and P. L. Palej. *Zhur. Neorg. Khim.*, 5 (1960) 31–34.
The oxidation–reduction tensions of the system Pu(III)/Pu(IV) in the presence of perchloric acid, hydrochloric acid and potassium chloride were determined potentiometrically, using the compensation method, in order to ascertain their dependence on the concentration of these monovalent electrolytes.
The redox tension of the system Pu(III)/Pu(IV) increases with increasing concentration of perchloric acid (from 0.5 to 4 *M* $HClO_4$). It decreases with increasing concentration of the chloride ion in solutions containing HCl (1–5 *M*), or HCl + KCl (1 *M* HCl + 0.5–3.8 *M* KCl), which points to the formation of complexes. The stability constants of $PuCl^{3+}$ and $PuCl^{2+}$ were found to be equal to 0.8 and 0.3 respectively, at room temperature. [Li.Ne.Ro.]

233 – Titrimetric determination of tungstate ions as lead tungstate (in German). H. Grubitsch, N. Ozbil and K. Kluge (Institute für Anorganische-Chemische Technologie und Analytische Chemie der Technischen Hochschule, Graz, Deutschland). *Z. anal. Chem.*, 166 (1959) 114–120.
The best conditions are given for the potentiometric and adsorptiometric end-point determination in the titration of tungstate with lead nitrate through the formation of a sparingly soluble lead tungstate. The tungstate solution is made slightly acid by adding HNO_3 and using 2–3 drops of 0.1% aqueous solution of the Na-salt of bromothymol blue as indicator; after a little boiling CO_2-free NaOH is added until a green colour is obtained: potentiometric titration is performed at 50° with stirring with 0.05 *M* lead nitrate solution. Electrodes can be W/sat. Hg_2Cl_2 or W/Pt; tungsten is used as an emery abrated wire. The lead solution is added drop by drop; near the end-point (tension change of 5–10 mV) 0.02 ml of solution are added every 30 sec. At the equivalence-point there is a sharp change of the tension (100–150 mV). Large quantities of neutral salts, complex-forming substances (acetate, tartrate, oxalate, citrate, phosphate, etc.) and carbonate, aluminate, plumbate, molybdate, chromate and vanadate must be absent. The titration with the adsorption indicator is carried out by adding 3–4 drops of 0.2% aqueous solution of amino-black-green B and of diamino-solid-scarlet 6 BS to 50 ml of the boiling solution. Without further heating the lead nitrate solution is added dropwise and the end-point is reached when the solution becames blue and the precipitate red. The end-point is very sharp for more than 30 mg of tungsten. The above-mentioned substances interfere. The average error for a single determination is about ± 0.1–0.2%. [G.deAn.]

234 – The stability and solubility of AgO in alkaline solutions. Thedford P. Dirkse and Brandon Wiers (Dept. of Chem., Calvin College, Grand Rapids, Mich., U.S.A.). *J. Electrochem. Soc.*, 106 (1959) 284–287.
By means of a potentiometric titration with KI reagent using a silver electrode against a saturated calomel comparison electrode, it was found that silver oxide is not affected by boiling water, but is very slightly decomposed at room temperature in strongly alkaline solution. The presence of Ag_2O in the alkaline solution does not affect this stability, whereas unoxidized silver increases the decomposition rate.
AgO dissolves in alkaline solution in the form of AgO or $Ag(OH)_3^-$. The equilibrium constant for the reaction: $AgO + OH^- + H_2O \rightleftharpoons Ag(OH)_3^-$, is given as $1.7 \cdot 10^{-4}$. The standard free energy of formation of $Ag(OH)_3^-$ is thus —85,380 cal/mole.
An attempt to explain the maximum observed in the solubility-curve of AgO in 4.75 *M* KOH at room temperature is made. [Fe.Jol.]

235 – Complex ions in fused salts. Silver halides. F. R. Duke and H. M. Garfinkel (Inst. for Atomic Research and Dept. of Chem., Iowa State University, Ames, Iowa ,U.S.A.). *J. Phys. Chem.*, 65 (1961) 461–463.
The system $AgNO_3$–KX in sodium–potassium nitrate eutectic solvent has been investigated by following the electrical tension as a function of the concentration of either chloride or bromide ion. Since the silver nitrate electrode shows Nernst behavior, the deviations from such behavior have been ascribed to complex ion formation. Several determinations have been made at various temperatures and equilibrium constants and standard heats of reaction have been tabulated for the different species postulated. [D.S.Ru.]

236 – Complex compounds of iridium(IV) with phosphoric acid (in Russian). N. K. Pshenitsyn, S. I. Ginzburg and L. G. Sal'skaya. *Zhur. Neorg. Khim.*, 5 (1960) 832–841.
Compounds of iridium(IV) have been synthesised as red–violet and blue coloured solutions by evaporation of the chloro-iridate or of the chloro-iridite with perchloric acid and phosphoric acids in the presence of oxidizers.
It was found that in perchloric acid, as well as in aqueous solutions of phosphoric acid in the presence of oxidizers, a bi- or polynuclear water-hydroxy compound of Ir(IV) is formed, this being first isolated as a sulphate. The composition and the chemical properties of this compound were determined by means of various analytical methods. The valence state of iridium in the isolated compound was established by potentiometric titration with ferrous ammonium sulphate hexahydrate.
On evaporating the red solution of the compound with phosphoric acid, a reaction takes place between the complex cation and the anions of the acid, in proportion to the increasing concentration of the latter, with the formation of a bi- or polynuclear complex anion. This was first isolated from the solution in the form of its ammonium, potassium, barium, silver and quinoline salts. The composition, chemical and some physico-chemical properties of these compounds were studied, mainly by applying the potentiometric titration method.
It was demonstrated, that the composition of the complex anion depends on the pH of the medium and the compounds obtained are acid salts of polybasic acids. [Li.Ne.Ro.]

237 – Formation of complexes of the uranyl ion with 8-hydroxyquinoline (in Russian). M. P. Pavlovskaya and I. M. Rejbel' (Dept. of Inorg. Chem., Kishinev Agricultural Inst., U.S.S.R.). *Zhur. Neorg. Khim.*, 5 (1960) 393–395.
In order to determine the composition of the complex compound formed by the uranyl ion with 8-hydroxyquinoline (in 2.66 mol CH_3COOH) in the presence of excess pyridine, the authors applied the method of potentiometric titration. The composition of the complex was found to correspond to the proportion UO_2^{2+} : 8-hydroxyquinoline = 1 : 1. [Li.Ne.Ro.]

238 – Basic chloride and hydroxide of samarium (in Russian). N. V. Aksel'rud and B.V. Spivakovskij (Inst. for General and Inorg. Chem., Academy of Sciences of the Uzbek S.S.R.). *Zhur. Neorg. Khim.*, 5 (1960) 340–347.
The composition, activity products and isobaric–isothermic formation potentials of the slightly soluble compounds ($Sm(OH)_2Cl$–$Sm(OH)_3$) formed by the addition of a sodium hydroxide solution to solutions of samarium chloride in the presence of sodium chloride at 25° were determined by measuring three variables, *i.e.*:

(a) the pH, using a glass electrode and a potentiometer type 'PPTV-1';
(b) the activity of the chloride ions, using a silver chloride electrode, or — in more concentrated solutions — a calomel electrode;
(c) the activity of the Sm^{3+} ions.

The latter values were calculated on the basis of an empirical function, correlating the composition of the solutions containing $SmCl_3$ and NaCl and the experimentally found activity coefficients of $SmCl_3$ solutions of different concentrations to the activity coefficients of $SmCl_3$ in the presence of NaCl. The composition of the compound in equilibrium with the solution in the freshly prepared system corresponded to the formula $Sm(OH)_2Cl$; after a month to $Sm(OH)_3$. The activity products of the precipitate, determined immediately and after one month were dependent on the activity of the chloride ions. [Li.Ne.Ro.]

239 – Basic chlorides and hydroxide of dysprosium (in Russian). N. V. Aksel'rud and V. B. Spivakovskij (Inst. for General and Inorg. Chem., Academy of Sciences of the Uzbek S.S.R.). *Zhur. Neorg. Khim.*, 5 (1960) 348–355.
The authors determined the composition, activity products and isobaric–isothermic formation potentials of dysprosium basic chlorides and hydroxide, which are formed in the system Dy^{3+}–OH^-–Cl^-–H_2O at 25°, by measurement of three variables, *i.e.*:

(a) the pH, using a glass electrode;
(b) The activity of the chloride ions, using a silver chloride or a calomel electrode;
(c) the activity of the Dy^{3+} ions.

The latter values were calculated on the basis of an empirical law, correlating the activity coefficients of $DyCl_3$ in solutions containing NaCl to the activity coefficients of dysprosium chloride in pure solutions.
When analysed soon after its formation, the precipitate was found to contain $Dy(OH)_{1.75}Cl_{1.25}$, $Dy(OH)_2\,Cl$ and $Dy(OH)_{2.5}Cl_{0.5}$; after ageing it consisted only of $Dy(OH)_3$. [Li.Ne.Ro.]

240 – Relationship between oxide films and electrode potentials. R. C. Plumb (Worcester Polytechnic Inst., Mass., U.S.A.). *Nuclear Sci. Abstr.*, 15 (1961) 343, Abstr. No. 2620.

241 – Hydrolysis of the uranyl ion, UO_2^{2+}, in perchlorate self-medium. Sirkka Hietanen and Lars Gunnar Sillen (Dept. of Inorg. Chem., Royal Institute of Technology, Stockholm 70, Sweden). *Acta Chem. Scand.*, 13 (1959) 1828–1838.
The hydrolysis of UO_2^{2+} has been studied in perchlorate self-medium at 25°, using quinhydrone or glass electrodes, which gave concordant results. The data indicate the two main reactions: $2\ UO_2^{2+} + H_2O \rightleftharpoons (UO_2)_2OH^{3+} + H^+$ (equilibrium constant β_{12}) and $2\ UO_2^{2+} + 2\ H_2O \rightleftharpoons (UO_2)_2\,(OH)_2^{2+} + 2\ H^+$ (equilibrium constant β_{22}). Small deviations at low acidities could be explained assuming the reaction $3\ UO_2^{2+} + 4\ H_2O \rightleftharpoons (UO_2)_3(OH)_4^{2+} + 4\ H^+$ (equilibrium constant β_{43}). The values obtained were: in the medium 0.4 M UO_2^{2+}, 1.0 M $(Na)ClO_4$, $\log \beta_{12} \rightleftharpoons -3.66 \pm 0.20$, $\log \beta_{22} = -6.02 \pm 0.03$. In 1.4 M UO_2^{2+}, 3.0 M $(Na)ClO_4$, $\log \beta_{12} = -3.68 \pm 0.20$, $\log \beta_{22} = -6.31 \pm 0.03$, $\log \beta_{43} \approx -12.6$ (quinh.), -12.9 (glass). The values for β_{22} and β_{43} are of the same order as obtained in an inert medium. The concentration of $(UO_2)_2OH^{3+}$ is appreciable only at high UO_2^{2+} concentrations. [Author]

242 – Stability of the titanyl oxalate complex in solution (in Russian). A. A. Grindberg and L. V. Shikheeva. *Zhur. Neorg. Khim.*, 5 (1960) 599–603.
The complex ion $[TiO(C_2O_4)_2]^{2-}$ undergoes dissociation in aqueous solution. The authors describe

the equilibria of two successive steps of dissociation and determine the instability constants. The first one, K_2, defined as

$$\frac{[TiO(C_2O_4)(H_2O)_2][C_2O_4]^{2-}}{[TiO(C_2O_4)_2]^{2-}},$$

was found to be equal to: (a) $0.77 \cdot 10^{-5}$ when determined by potentiometric titration with hydrochloric acid; (b) $4 \cdot 10^{-5}$ when determined by means of the mercuric oxalate electrode. (The latter was preferred to the silver oxalate electrode, due to the extremely low concentration of the ions $C_2O_4^{2-}$). The second one, K_1, defined as

$$\frac{[TiO(H_2O)_4]^{2+}[C_2O_4]^{2-}}{[TiO(C_2O_4)(H_2O)_2]},$$

was approximatively determined, its value being $2 \cdot 10^{-10}$. [Li.Ne.Ro.]

243 – Equilibria in ethylenediamine. I. The relative dissociation constants of silver salts and alkali metal halides. Stanley Bruckenstein and L. M. Mukherjee (School of Chem., University of Minnesota, Minneapolis, Minn., U.S.A.). *J. Phys. Chem.*, 64 (1960) 1601–1607.
Cells of the type, comparison electrode//$AgX(C_1)Ag$ and comparison electrode//$AgX(C_1)$, $MX(C_2)/Ag$ were used to determine the relative dissociation constants of a series of silver salts and alkali metal halides in ethylenediamine. The values of pK_{AgCl}-pK_{MX} for the specified MX were: LiCl, —0.33; NaCl, —0.18; KCl, —0.01; RbCl, +0.03; CsCl, +0.22; AgBr, —0.63; LiBr, —0.67; NaBr, —0.50; KBr, —0.72; RbBr, —0.69; CsBr, —0.60; AgI, —1.35; LiI, —0.46; NaI, —0.24; KI, —0.23; RbI, —0.42; CsI, —0.36; $(n\text{-}C_4H_9)_4NI$, —0.44; AgOAc, +0.88; AgSCN, +1.03; and $AgNO_3$, +1.34. Silver iodide reacts according to the equation $AgI + MI \rightleftharpoons AgI.MI$ with the following equilibrium constants for sodium, potassium, rubidium and caesium iodides 1.33, 1.13, 1.60 and 1.58 respectively. [D.S.Ru.]

See also abstracts nos. 2, 7, 11, 12, 20, 29, 37. 38, 58, 151, 153, 348.

5. Conductometry

244 – Physicochemical studies of some cyclic carbonates. III. Electrical conductivities in ethylene carbonate. R. F. Kempa and W. H. Lee (Battersea College of Technology, London, Great Britain). *J. Chem. Soc.*, (1961) 100–105.
Conductometric measurements on various 1–1 electrolytes of sufficiently high solubility (alkali metal perchlorates and tetraalkylammonium halides) have been made in ethylene carbonate, which has been found to be a good ionising medium. (This solvent has a dielectric constant of 89.6 at 40° and is probably only slightly associated in contrast with water or N-monomethyl amides.) Negative and positive deviations from the theoretical Onsager lines in Kohlrausch diagrams are attributed respectively to extensive solvation of the smaller cations, and, to some extent, to ion-pair formation. Approximate solvation numbers calculated from apparent ionic radii increase in the following sequence: Cs^+ (1.7), Rb^+(2.2), K^+(2.5), Na^+(4), Li^+(6). [L.Gi.]

245 – Conductometric determination of copper (in Russian). G. B. Pasovskaya. *Izvest. Akad. Nauk Turkmen. S.S.R.*, (1959) 73–74.
Cu (as Cu^{2+}) can be determined in brass and bronze by conductimetric titration with $Na_2S_2O_3$, in the presence of Fe^{3+}, Al^{3+}, Zn^{3+}, Mn^{2+}, Pb^{2+} and Sn^{4+}.
The sample is dissolved in HNO_3, the solution evaporated in a water bath, then cooled and the residue redissolved in water. The solution obtained is titrated in a conductimetric apparatus with thiosulfate after addition of a small quantity of solid NH_4F to eliminate Fe^{3+}. Cu^{2+} is titrated before Zn when approximately equal amounts of the two are present. When the amount of Zn

is too small, some $ZnSO_4$ is added to facilitate the interpretation of the titration curve. The error is less than 0.1% even if the concentration of Cu is as small as 0.5 mg in 25 ml of solution. [Gio.Ser.]

246 – Analysis of mixtures of sulphuric and nitric acids. Conductimetry (in French). Y. Lacroix and M. Chaverou. *Mém. poudres*, 41 (1959) 423–439.

A conductimetric apparatus is described which enables the sample temperature to be controlled within ±0.1°. It uses bright platinum electrodes and a Wheatstone bridge operating at 1000 c/sec. The use of the apparatus for the analysis of mixtures of H_2SO_4, HNO_3 and water is discussed. The precision of the apparatus described is 0.1%, but with the above-mentioned mixtures in process samples analysis, the values obtained are 5% low, probably due to organic impurities. [Gio.Ser.]

247 – The conductance of ferric and cupric stearates in aliphatic hydrocarbons. C. M. French and E. R. Monks (Queen Mary College, Mile End Road, London, Great Britain). *J. Chem. Soc.*, (1961) 466–468.

In spite of the considerable irreproducibility of the measurements from some systems, the following facts have emerged:
(1) ionisation, though not extensive, does occur;
(2) the molar conductances of all solutions of ferric stearate are greater than the corresponding solutions of cupric stearate (up to 10-fold for anhydrous, and up to 100-fold for moist solutions);
(3) addition of 2 moles of water per mole of solute affects only the ferric stearate solutions (10-fold increase of conductance);
(4) change in the nature of the solvent exerts only a minor influence;
(5) conductances generally increase with temperature.

It is suggested that the lack of uniformity in conductometric behaviour from system to system is caused by the formation of micelles with subsequent adsorption of ions. The effect of small traces of water is probably associated with the hydration of the solute molecules, followed by their hydrolysis. [L.Gi.]

248 – The conductance of solutions in which the solvent molecule is „large". VII. Solutions in triaryl phosphites. C. M. French and R. C. B. Tomlinson (Queen Mary College, Mile End Road, London, Great Britain). *J. Chem. Soc.*, (1961) 311–320.

The conductances of four tetraalkylammonium toluene-*p*-sulphonates (methyl, ethyl, *n*-propyl, *n*-butyl) have been measured in various phosphites (triphenyl, tri-*m*-toluyl, tri-*p*-toluyl, tri-*p*-ethylphenyl) over a concentration range from $6.0 \cdot 10^{-6}$ to $7.9 \cdot 10^{-3}$ *N*. The general behaviour can be explained in terms of ion-pair and triple-ion formation, with negligible ion-atmosphere effects. It is suggested that the extremely low values of conductance, and the occurrence of certain apparently anomalous variations of association constants, could be accounted for by ion–dipole and ion pair–solvent interactions. These interactions depend on both the dipole moment and the geometry of the solvent molecules. (Infrared spectra indicate that aryl phosphites tend to adopt a planar configuration.) [L.Gi.]

249 – High frequency titration of hydroxy-tetracycline and its hydrochloride (in German). G. Löber and G. Heese (Inst. for Microbiol. and Exptl. Therapy, Jena, and Academy of Science, Berlin, Germany). *Pharmazie*, 14 (1959) 214–217.

A 350 mg sample of the hydrochloride is precipitated in a specially designed cell (made from Condensa-F and able to contain as much as 8 times the quantity contained in normal cells with a similar volume) with 6 ml 3% mercuric acetate; titration is then carried out with 0.1 *N* perchloric acid in acetic acid (acetic anhydride is not necessary).

A correction factor $F = -0.0011(t\text{-}20)$ must be used if the temperature, t, is $\neq 20°$.

Owing to the larger amount of product titratable, the errors of the method described (0.2%) are five times lower than in visual or potentiometric titrations. [Ca.Cas.]

250 – The use of conductometry for the direct microdetermination of oxygen in organic compounds (in Russian). N. E. Gelman, Van Ven-Iun and I. I. Bryushkova (Institute of Element–Organic Compounds, Academy of Sciences, U.S.S.R.). *Zavodskaya Lab.*, 27 (1961) 24–30.

The sample is decomposed at 900° in an atmosphere of nitrogen or argon in an oven in which oxygen is simultaneously converted to carbon monoxide over a platinum catalyst. The gaseous reaction products are then carried by the inert gas to a column on which the CO is oxidised to CO_2, which is finally absorbed in hydroxide solution, the conductivity of which is measured. A drawing of the apparatus and a wiring diagram are included. [Ot.So.]

251 – Conductimetric titration of *iso*-humolone in beer according to Verzele (in German). H. Egner (Brauerei Rob. Leicht A.G., Stuttgart-Vaihingen, Germany). *Brauwissenschaft*, 13 (1960) 39–40.
The method described is laborious and cumbersome, but can be used with success when a spectrophotometer is not available and also gives results in good agreement with those from previously known methods. [Gio.Ser.]

252 – Electrical conductivity of some organic solutes in anhydrous hydrogen fluoride. Lloyd Quarterman, Herbert H. Hyman and Joseph J. Katz (Argonne National Laboratory, Argonne, Ill., U.S.A.). *J. Phys. Chem.*, 65 (1961) 90–93.
Many organic liquids containing oxygen are miscible with anhydrous hydrogen fluoride. Ethanol, acetic acid and diethyl ether are typical proton acceptors and form highly conducting solutions over most of the concentration range. Trifluoroethanol, trifluoroacetic acid and nitrobenzene are much less extensively ionized in this medium. Perfluorobutyl ether is essentially insoluble. The electrical conductivities for these systems are tabulated and compared. [D.S.Ru.]

253 – Comparisons of electrometric measurements in clay systems. K. B. Deshpande and C. E. Marshall (Dept. of Soils, University of Missouri, Columbia, Miss., U.S.A.). *J. Phys. Chem.*, 65 (1961) 33–36.
Measurements of salt activity, cation activity and low and high frequency conductance have been made on potassium and calcium montmorillonite clay systems. The results from the three methods for dilute clay systems indicate: (1) that cation activity determinations are not measurably affected by tensions at the junction of the KCl bridge and colloidal clay; (2) that cations in the diffuse part of the double layer have normal mobilities, whereas those in the Stern layer have zero mobility in d.c. conductance and normal mobility at high frequencies. Chemically adsorbed ions showing neither activity nor conductance are also present. [D.S.Ru.]

254 – Determination of alkaloids by high-frequency titration (in Spanish). F. E. Raurich Sas and A. Tarrès Torras (Inst. Alonso Barba, C.S.I.C., Barcellona, Spain). *Inform. quim. anal. (Madrid)*, 14 (1960) 1–19.
A review of the methods and apparatus used in high-frequency titrations is given and the principles involved are discussed.
The titration of alkaloid salts by this method, using 0.1 *N* NaOH is described. The results from samples of 10 mg are shown to be in agreement with theoretical values within 2–3%. [Gio.Ser.]

255 – Distinction between refined and unrefined olive oils. E. Lauber (Health Office, Bern, Switzerland). *Mitt. Lebensm. Hyg.*, 50 (1959) 553–566.
Unrefined oils have a greater conductivity than refined ones because of the higher acidity and the presence of phosphatides. A special cell for the measurement of the electrical conductivity of the oils has been constructed and used. 35–40 ml samples are required and the measurements must be made at exactly 100°C.
Absorption curves may also be correlated to the degree of refining of the oils, by measuring the extinction at 500 mμ. Chlorophyll causes a peak at 670 mμ, which decreases highly in refined oils. [Gio.Ser.]

256 – The evaluation of conductometric titrations (in German). F. Oehme (Institut Entw. chem.-phys. Analysenmeth., Weilheim/Obb., Deutschland). *Mitt. Inst. Entw. chem.-phys. Analysenmeth.*, 4 (1960) 96–100.
Die Bestimmung des Endpunktes konduktometrischer Titrationen erfolgt auch heute noch durch geeignete graphische Auswertung eines Titrations-Diagrammes (das entweder mit den Messwerten gezeichnet oder mit registrierenden Geräten geschrieben wird). Es gibt jedoch Möglichkeiten, ohne diese Diagramme auszukommen. Das gilt speziell für die ,,Überpunktmethode'' von Spillner und Voigt (*Angew. chem.*, 66 (1954) 198.). Hierbei wird das (direkt anzeigende) Leitfähigkeitsmessgerät als Indikator benutzt. Titrationsmittel wird solange zugegeben, bis der ,,Überpunkt'' erreicht ist. Eine ganz einfache Volumenkorrektur liefert den Äquivalenzpunkt mit grosser Genauigkeit. Die methodischen Voraussetzungen dieser Methode werden kurz diskutiert und mit Beispielen belegt. Ein Sonderfall einer rechnerischen Auswertung wird für Titrations-Diagramme beschrieben, welche keinen scharfen Knick, sondern ein gekrümmtes Übergangsgebiet aufweisen (E. Grunwald, *Anal. Chem.*, 28 (1956) 1112). Eine einfache Zwischenrechnung liefert die Gleichung zweier Geraden, welche durch Gleichsetzen der unabhängigen Veränderlichen den Verbrauch des Titrationsmittels für den Äquivalenzfall ergeben. [Fr.Oe.]

257 – Variation en fonction de la température de la conductibilité de l'acide acétique à faible teneur

en eau. G. Perrault et J. Brenet (Laboratoire de Chimie-Physique du Corps solide, Faculté des Sciences, Strasbourg, France). *Compt. rend.*, 252 (1961) 104–106.
Les Auteurs ont déterminé, en fonction de la température, la conductibilité de mélanges acide acétique–eau à faible teneur en eau ($H_2O < 15\%$). De ces mesures on déduit les énergies d'activition E définies par $\lambda = \lambda_0 e^{-} E/kt$. Les courbes $\log \lambda = f(1/T)$ se scindent en plusieurs segments de droites parallèles reliées par des zones de température (θ température moyenne de la zone) où la variation d'énergie est plus rapide. Les Auteurs reportent les variations de la température θ en fonction de la composition du milieu, c'est-à-dire de la concentration de l'eau dans l'acide acétique et en déduisent certaines conclusions en ce qui concerne la formation de composés d'association entre l'acide et l'eau. L'énergie E est voisine de 0.12 eV si la concentration de l'eau est supérieure à 6%. Pour des concentrations plus faibles, elle augmente rapidement jusqu'à 0.22 eV pour de très faibles teneurs en eau. Cette augmentation serait due au remplacement des ions $(H_2O)_4H^+$ par les ions $CH_3CO_2H_2^+$. [Bad.Lam.]

258 – **Conductometric study on the precipitation of arsenites of silver as a function of pH.** R. S. Saxena and C. S. Bhatnagar (Chem. Lab., Government College, Kota, Rajastan, India). *Naturwissenschaften*, 46 (1959) 575.
The formation and composition of silver arsenites, obtained by interaction of $AgNO_3$ and $NaAsO_2$ has been studied at pH 9.85, 11.25 and 12.28 in conductivity water at 30 ± 1°. By mixing $NaAsO_2$ (pH = 9.85) with NaOH (1 : 1 and 2 : 1) $Na_4As_2O_5$ at pH 11.25 and Na_3AsO_3 at pH 12.28 were formed. By conductometric titration with $AgNO_3$ the formation of the corresponding silver arsenites was proved. Addition of alcohol improves the end-point by decreasing the adsorption of AsO_2^- and the solubility of the silver arsenites. [H.W.Nür.]

259 – **The equivalent conductivity of aqueous $CuCl_2$- and Na_2SO_4- solutions at 25°C** (in German). M. Kahlweit (Max-Planck-Institut f. physikal. Chemie, Göttingen, Deutschland). *Z. physik. Chem. (Frankfurt)*, 27 (1961) 297–298.
Data concerning the specific conductivity κ and the equivalent conductivity Λ are given including the limiting values Λ_0 calculated by Onsager's equation. For $CuCl_2$, κ reaches a maximum far below the concentration of the saturated solution, while κ for Na_2SO_4 has its maximum at a concentration higher than that of the saturated solution. [H.W.Nür.]

260 – **Relationships between electrical resistance and the hydrogen content of palladium.** T. B. Flanagan and F. A. Lewis (Chemistry Dept., Queen's University, Belfast, N. Ireland). *Z. physik. Chem. (Frankfurt)*, 27 (1961) 104–111.
Results obtained by an improved experimental method for measuring the relationship between H/Pd (atomic ratio) and R/R_0 (R_0 is the resistance of hydrogen-free Pd) are given. Also the temperature coefficient of R is determined between 0 and 55°C. [H.W.Nür.]

261 – **Physico-chemical analysis of aqueous solutions of the phosphoric acid–sulfuric acid system.** (in Russian). D. P. Belotskij and M. F. Khokhol (Chernovits State University, U.S.S.R.). *Zhur. Neorg. Khim.*, 5 (1960) 708–712.
Mixtures of phosphoric acid and sulfuric acid in aqueous solution, with total concentrations of 1 and 13.8 mol/l were analysed, at 25° and 45° by means of physico-chemical methods, including measurements of density, viscosity and electrolytic conductance.
All the data obtained point to the presence of a chemical compound $(H_4PO_4)^+HSO_4$ in the solutions which contain the acid components in a 1 : 1 proportion. [Li.Ne.Ro.]

262 – **Transport numbers and ionic mobilities in the system potassium chloride–lead chloride.** Frederick R. Duke and Richard A. Fleming (Institute for Atomic Research and Dept. of Chem., Iowa State College, Ames, Iowa, U.S.A.). *J. Electrochem. Soc.*, 106 (1959) 130–133.
The ionic transport numbers and ionic mobilities were determined for the fused potassium chloride–lead chloride system. The cation transport numbers were: 0.24 for $PbCl_2$ at 525° and 0.62 for KCl at 850°. In each mixture, t_- (transport number of Cl^- ion) deviated positively and t_+ and t_{2+} (transport number of K^+ ion and Pb^{2+} ion, respectively) deviated negatively from linearity when plotted against the equivalent fraction. Addition of small amounts of $PbCl_2$ to pure KCl cause a very rapid decrease of the total equivalent conductance. This effect was found to be due to a diminution of the ionic conductance of K^+ rather than complexing between Pb^{2+} and Cl^-. The relative mobilities of K^+ and Pb^{2+} were compared with those of Li^+ and Pb^{2+} in the system $LiCl-PbCl_2$ calculated from literature data. [Fe.Jol.]

263 – **The second (rapid) step in the nucleophilic substitution of alkyl halides. I. Hydrolysis of triphenylmethyl chloride in acetone of low water content.** D. Golomb (Weizmann Institute of Science, Rehovah, Israel). *J. Chem. Soc.*, (1959) 1327–1333.

It has been shown conductometrically that hydrochloric acid dissociates only slightly in acetone of low water content (*Ka* in water–acetone (3%–97%) at 29.5° $\cong 2\cdot10^{-4}$). Therefore the hydrolysis of triphenylmethyl chloride in this medium follows the first-order kinetic law strictly since the concentration of chloride ion will not rise to a level sufficient to reverse reaction (a) in the hydrolysis scheme:

$$\text{(a)}\quad Ph_3C\cdot Cl \rightleftharpoons Ph_3C^+ + Cl^-$$
$$\text{(b)}\quad Ph_3C^+ + H_2O \rightarrow Ph_3C.OH + H^+.$$

The addition of lithium chloride, however, causes a decrease in the first-order rate constant. It was found that the dissociation of lithium chloride is 8 times that of hydrochloric acid in this medium, so that a higher chloride ion concentration is present to retard hydrolysis. Perchloric acid and lithium perchlorate retard the reverse reaction in step (a) above because of the primary salt effect, and therefore increase the overall rate of hydrolysis. Silver nitrate reduces the chloride concentration and thus also causes an increase. Increase in the water content of the acetone increases its ionizing power and enhances the dissociation in step (a). In heavy water the rate constant is depressed. [G.F.Rey.]

264 – Thermodynamics of the monohydrogen difluorides. I. Decomposition reaction, fusion, phase transition and electrical conductivity of β-potassium monohydrogen difluoride. Merton L. Davis and Edgar F. Westrum, Jr. (Dept. of Chem., University of Michigan, Ann Arbor, Mich., U.S.A.). *J. Phys. Chem.*, 65 (1961) 338–344.
The thermophysical properties of β-KHF_2 were determined. The electrical conductivity of α, β and liquid KHF_2 were measured. It was difficult to obtain reproducible data due to supercooling in the α-phase. In the β-region the conductivity $= 1.15\cdot10^5 \exp(-1.05\cdot10^4/T)$. [D.S.Ru.]

265 – Potassium hexafluorophosphate — An associated electrolyte. R. A. Robinson, J. M. Stokes and R. H. Stokes (Chem. Dept., University of New England, Armidale, N.S.W., Australia). *J. Phys. Chem.*, 65 (1961) 542–546.
The densities, viscosities and conductances of aqueous solutions of potassium fluorophosphate have been determined at 25 and 50°. Isopiestic vapor pressure measurements have been made at 25° and the osmotic and activity coefficients computed. The equivalent conductances at infinite dilution are 132.83 and 203.25 cm^2int. ohm^{-1} $equiv^{-1}$ at 25 and 50°, respectively, and the association constants are 2.42 and 1.43 liter mol^{-1}. [D.S.Ru.]

266 – Physico-chemical study of the interactions of thorium nitrate with phenylacetic acid (in Russian). K. N. Kovalenko and M. N. Tarasova (Rostov-on-Don State University, U.S.S.R.). *Zhur. Neorg. Khim.*, 5 (1960) 385–392.
A detailed investigation of the system thorium nitrate–phenylacetic acid in aqueous solution has been carried out by the authors, who applied the method of continuous variations according to Ostromyslenskij–Zhob. Measurements of conductance, pH and surface tension in the liquid phase of the system enabled them to establish that an exchange reaction takes place between thorium nitrate and phenylacetic acid in aqueous solutions with the formation of a poorly-soluble thorium salt, $(C_6H_5CH_2COO)_4Th$. No other compounds of different composition were detectable. [Li.Ne.Ro.]

267 – Study of the formation of complexes in the system VO^{2+}–CNS^-–solvent (in Russian). A. M. Golub and R. A. Kostrova. *Zhur. Neorg. Khim.*, 5 (1960) 726–730.
The formation of complexes in the system VO^{2+}–CNS^-–solvent has been studied by spectrophotometric and conductometric methods. The conductometric measurements were performed at 20° on aqueous and aqueous–acetonic solutions (50% acetone) of vanadyl sulphate and potassium thiocyanate, prepared by using the principle of isomolar series.
The introduction of non-aqueous solvents favours the formation of anionic complexes up to $VO(CNS)_4^{2-}$. Complexes such as $VOCNS^+$ and $VO(CNS)_2$ were revealed, however, in the aqueous solutions. [Li.Ne.Ro.]

268 – The existence of hexachlorogermanates, M_2GeGl_6. T. C. Waddington and F. Klanberg (Chem. Lab., University of Cambridge, Great Britain). *Naturwissenschaften*, 46 (1959) 578.
By conductometric titration of tetraalkyl ammonium chlorides of $GeCl_4$ dissolved in anhydrous HCl no formation of $GeCl_6^{2-}$ could be found. Liquid $GeCl_4$ itself neither dissolves any chloride ion donors nor reacts with them as was proved by a number of other methods. In contrast $SnCl_4$ forms $SnCl_6^{2-}$ ions, as was shown by conductometric titration. [H.W.Nür.]

269 – Rapid method for the detection of the basicity of Siemens–Martin slags (in German). H. vom Ende and F. Bardenheuer (Metallurg. Abt., Mannesmann AG, Hütte, Huckingen, Duisburg, Deutschland). *Arch. Eisenhüttenw.*, 30 (1959) 391–396.

Ein Schellverfahren zur konduktometrischen Bestimmung der Basizität wässriger Suspensionen von Schlackenpulvern bei 80° und konstanter Rührung wird beschrieben. Einfluss von Temperatur, Korngrösse und Konzentration werden studiert. Nach der angegebenen Arbeitsvorschrift ist in 6 min nach Probeneingang die Analyse durchzuführen. [H.W.Nür.]

270 – The conductometric determination of carbon in beryllium. E. M. Massey (Union Carbide Nuclear Co., Oak Ridge, Tenn., U.S.A.). *Nuclear Sci. Abstr.*, 15 (1961) 341, Abstr. No. 7599. [Red.]

271 – Determination of free acid in highly radioactive solutions by remotely controlled conductometric titration. R. E. Corcoran, H. E. Zittel, S. R. Dinsmore and U. Koskela (Oak Ridge Natl. Lab., Tenn., U.S.A.). *Nuclear Sci. Abstr.*, 15 (1961) 339, Abstr. No. 2585. [Red.]

See also abstracts nos. 3, 4, 28, 51, 52, 61, 62, 153, 177, 231.

6. Electrolysis

272 – Potentiostatic isolation of structural components of nickel alloys (in German). Ch. Ilschner-Gensch (Fa. Krupp, Essen, Deutschland). *Arch. Eisenhüttenw.*, 31 (1960) 97–102.
Passivität der Grundmasse und geringe elektrochemische Potentialunterschiede der Gefügebestandteile machen den Einsatz eines elektronisch regelnden Potentiostaten erforderlich. Geeignete Spannungen zur Auflösung bestimmter und damit zur Isolierung anderer verbleibender Phasen werden durch vergleichende Auswertung von Strom–Spannungs-Kurven ermittelt, die an makroskopischen Proben reiner Phasen, die im Gefüge der zu untersuchenden Proben vermutet werden, gemessen wurden. [H.W.Nür.]

273 – Three-dimensional representation of electrodeposition. W. H. Reinmuth (Columbia University, New York, U.S.A.). *J. Chem. Ed.*, 38 (1961) 148.
A three-dimensional space model is used to illustrate the principles of electrometric and voltametric processes. Current, electrical tension and per cent oxidation are the three axes used. [D.S.Ru.]

274 – The isolation and analysis of oxides included in steel (in German). S. Meyer and O. G. Koch (Chem. Lab., Neunkircher Eisenwerk AG, Neunkirchen/Saar, Deutschland). *Arch. Eisenhüttenw.*, 31 (1960) 651–657.
Möglichkeiten zur Durchführung elektrolytischer Isolierungen ohne Schutzgas werden untersucht. Man kann (1) das anodisch gelöste Eisen mit Ionenaustauschern entfernen, (2) Elektrolytoberfläche durch Abdecken mit Lackfilm vor Luftsauerstoff schützen, (3) der Elektrolytlösung Reduktionsmittel zusetzen (Hydroxylaminhydrochlorid oder Hydrazinsulfat sind sehr geeignet). Am einfachsten und günstigsten erwies sich das 3. Verfahren. Weiter werden Arbeitsweisen erörtert, die zur Erzielung besserer Durchschnittswerte auf eine gleichmässige elektrolytische Eisenablösung über den ganzen Probenquerschnitt hinzielen. [H.W.Nür.]

275 – Role of thiourea in the electrodeposition of copper. Bacon Ke, John J. Hoekstra, Bienvenido C. Sison, Jr. and Dan Trivich (Dept. of Chem., Wayne State University, Detroit, Mich., U.S.A.). *J. Electrochem. Soc.*, 106 (1959) 382–388.
X-ray diffraction methods have shown that, in the presence of thiourea in an acid bath, a bright polycrystalline deposit of copper is obtained over the entire surface of the electrode formed by a spherical single copper crystal. In the absence of thiourea the copper forms single-crystal deposits on the (III) regions of the spherical electrode. By the use of S-35 labelled thiourea it was shown that this compound is strongly but fairly uniformly adsorbed on the spheres and that no preferential adsorption on crystal faces occurs. [Fe.Jol.]

276 – Separation of the lanthanons at amalgam cathodes. IV. High purity ytterbium from mixtures of heavy lanthanons by aqueous electrolysis. E. I. Onstott (University of California, Los Alamos Scientific Laboratory, N. Mex., U.S.A.). *J. Am. Chem. Soc.*, 82 (1960) 6297–6298.
The author has continued the investigation of the separation of the lanthanon elements by electrolysis at lithium mercury amalgam cathodes. Conditions suitable for the separation of ytter-

bium have been studied. Electrolysis of an oxide mixture of 31% Yb_2O_3, 51% Lu_2O_3, 7.3% Tm_2O_3, 6.2% Er_2O_3, and 4.3% Ho_2O_3 at 0.2 A/cm^2 from 1 *M* lithium citrate solution (using an initially pure mercury cathode) yielded quantitatively Yb in $>$ 99.9% purity. Similar electrolysis experiments were performed on a 50–50 oxide mixture of Yb and Tm at three pH values (6, 8, and 11). The rate of electrolysis decreased rapidly with decreasing solution acidity. Using radiotracer Tm, the separation factor was shown to be greater than 7,000; 99.98% pure Yb was obtained in the electrolysis at pH 6. Rather long electrolysis times were required for these experiments. [R.Mur.]

277 – Electrolytic separation of trace amounts of uranium, neptunium, plutonium and americium (in Russian). A. G. Samartseva. *Atomnaya Energiya*, 8 (1960) 324–329.
The use of a platinum foil cathode rotating at 60–80 rev/min and of a platinum dish as the anode eliminates the absorption of radioactive elements by the glass or plexiglass walls of electrolytic cells. The deposition takes place on both sides of the cathode, the α-activity of which is recorded by means of a special counter. Test solutions containing $1.3 \cdot 10^{-8}$ *M* ^{233}U, 0.2–$1.2 \cdot 10^{-6}$ *M* ^{239}Np, $4.1 \cdot 10^{-9}$ *M* ^{239}Pu and $1.4 \cdot 10^{-10}$ *M* ^{241}Am were used. HNO_3, HCl, $HClO_4$, H_2SO_4 and oxalic acid with H^+ concentrations ranging from 10^{-1} to 10^{-4} *M*, and buffered solutions with H^+ concentrations 10^{-5} to 10^{-9} *M* were used as electrolytes. The yield of the elements obtained by electrolysis depends only on the pH of the solution and not on the anion. Analysis of the elements recovered by suitable methods shows that ^{239}Pu contains less than 1% of ^{241}Am and ^{238}Pu, ^{237}Np contains *ca.* 2% of ^{239}Pu, ^{241}Am contains no impurity, while ^{233}U was not analysed. The valency-states of the elements in solution was been studied. Curves and tables are given and a method for the separation of Pu from the other elements is described. [Gio.Ser.]

278 – Effect of temperature on the rate of electrodeposition of zinc from sulphate solutions (in Russian). G. A. Emelyanenko (State University, Dniepropetrovsk, U.S.S.R.). *Zhur. Fiz. Khim.*, 35 (1961) 393–396.
The effect of temperature on the polarisation and rate of electrodeposition of zinc from sulphate solutions has been investigated. The cathodic polarisation for a given current density was found with increasing temperature to show an inflection point at a characteristic temperature. The nature of the $\log i$ — $1/T$ function was shown to change with the polarisation, duration of electrolysis, and temperature. In the initial moments when the process is not complicated by large values of concentration polarisation one may observe the linearity of this relation characteristic of electrochemical polarisation. The bending of the curve $\log i$ — $1/T$ towards the $1/T$ axis is explained by decrease in the contribution of electrochemical polarisation and increase in the contribution of concentration polarisation to the overall electrode polarisation values. [Ot.So.]

279 – Anodic behaviour of tin and zinc in alkaline electrolytes (in Russian). M. E. Prostakov, A. I. Levin and V. P. Kochergin (Polytechnic Inst., Sverdlovsk, U.S.S.R.). *Zhur. Fiz. Khim.*, 35 (1961) 420–425.
The anodic behaviour of tin and zinc in alkaline solutions and in solutions containing sodium chromate and potassium bromate has been investigated. With increase in solution temperature and in NaOH and $KBrO_3$ contents, the current density required to start the passivation of tin and zinc increases. On the other hand, addition of sodium chromate to the solution in amounts up to 20 g/l facilitates passivation of the metals. The behaviour of tin and zinc towards passivation in alkaline electrolytes showed that adsorption phenomena are of great importance in the process and considerably affect the ionization kinetics of the metals. [Ot.So.]

280 – Effect of SO_2 additions on the electrolysis and properties of manganese deposits (in Russian). A. T. Sanzharovskii (Inst. of Phys. Chem., Academy of Sciences, U.S.S.R. *Zhur. Phys. Khim.*, 35 (1961) 20–25.
A study has been made of the effect of SO_2 additions on the electrolysis of manganese under various conditions. Three different effects due to SO_2 addition have been established, depending on the pH value of the solution. At pH values above 6.0 SO_2 has no influence on the course of the electrolysis since it does not exist in the free state under these conditions. At pH's below 6.0 the presence of SO_2 causes chemical reactions as a result of which Mn(IV) and Mn(III) ions are reduced to Mn(II). At pH values below 4.0 SO_2 not only participates in the chemical reactions, but also takes part in the electrode processes, thus bringing about an increase in polarization of the cathode, inclusionof sulphur in the deposit and the appearance of "growth texture". Under these conditions considerable changes take place in the mechanical properties of the deposit. [Ot.So.]

281 – Electrolysis of non-aqueous tin halide solutions (in Russian). Yu. N. Volnov. *Zhur. Fiz. Khim.*, 35 (1961) 90–93.
The electrolysis of tin chloride, bromide and iodide in ethyl and butyl alcohols, acetic and butyric

acid, ethyl and butyl acetate and acetoacetic ester has been investigated with the object of obtaining a fuller picture of the structure of tin halide compounds. It was found that the solvent molecules travel toward the anode, whereas the tin and halogen ions are transported both to the anode and to the cathode, thus confirming the mechanism proposed by Miskidhyan for the dissociation of complex tin halide compounds. [Ot.So.]

282 – Determination of the reaction mechanism of the electrolytic formation of hydrazobenzene from nitrobenzene by the aid of controlled tension electrolysis (in Japanese). Taro Sekine and Tadashi Seki (Lab. of Org. Electrochem., Dept. of Chem. Eng., Tokyo Institute of Technology, Japan). *J. Electrochem. Soc. Japan*, 27 (1959) 332–338.
In order to verify the proposed mechanism for hydrazobenzene formation at the surface of a soluble cathode in alkaline emulsions, controlled tension electrolysis was carried out for the reduction of azoxybenzene and azobenzene at zinc and nickel cathodes. An instrument for controlled tension electrolysis was constructed for this purpose. The experiments were repeated for the same reductions in alcoholic alkaline solutions at a nickel cathode in order to confirm the mechanism proposed by Haber.
It was confirmed from the results that azoxybenzene did not form azobenzene as an intermediate product, but was reduced directly to hydrazobenzene in alcoholic alkaline solution. [Ta.Fu.]

283 – Anodic solution rate of nickel in nitric acid (in Russian) A. I. Falicheva and R. I. Tsyfanova (Polytechnic Inst. Sverdlovsk, U.S.S.R.). *Zhur. Fiz. Khim.*, 35 (1961) 350.
The effect of nitric acid concentration, anodic current density and temperature on the rate of solution of nickel in nitric acid has been investigated. The maximum solution rate was found to occur in 8.17 N nitric acid at 40° and $d_A = 750$ A/cm^2. The influence of the above factors on the amount of ammonium salts formed during the anodic solution of nickel in nitric acid was ascertained. Polarization curves were obtained during the solution process. It was found that the polarization curves for 3.17 and 3.78 N nitric acid consist of two branches, the first corresponding to the ionization of Ni^0 to Ni^{2+} and the second (following a current drop and tension jump) to oxygen evolution and the formation of higher valency nickel ions, probably Ni^{3+}. [Ot.So.]

See also abstracts nos. 18, 19, 33, 34, 57, 66, 113, 121, 153, 346.

7. Coulometry

284 – Determination of the stoichiometry of uranium dioxide by controlled potential coulometry. R. W. Strohmatt and R. E. Connally (General Electric Co., Richland, Wash., U.S.A.). *Anal. Chem.*, 33 (1961) 345.
In this investigation the ratio U/O is determined by controlled tension coulometry. After a short pre-electrolysis step the U(VI) of the original sample is reduced at —0.38 V *vs.* S.C.E. The U(IV) is then oxidized with Ce(IV) and after removing excess ceric ion the total amount of uranium is determined by reduction. The current–time function is integrated and written out by a recorder. The instrument is a modified type of the instrument described by Kelley. The dissolution procedure is carried out under a helium atmosphere to prevent oxidation. A 0.5 g sample is dissolved in 20 ml 85% phosphoric acid. All the reagents are deaerated. 80 ml 1 M sulfuric acid are added after heating and the resulting solution diluted to 100 ml with water. 1 ml is added to 10 ml 1 M sulfuric acid in the electrolysis vessel and the sample is first pre-reduced at +0.05 V, and then reduced at —0.38 V. The procedure gives the amount of U(VI) present. Twice the amount of ceric sulfate necessary to oxidize the uranium(IV) is added. After 3 min the sample is pre-reduced and reduced as before. The number of coulombs is then corrected for the blank. [Kl.Gr.]

285 – Application of stripping analysis to the determination of iodide with silver microelectrodes. I. Shain and S. P. Perone (Dept. of Chem., University of Wisconsin, Madison, Wis., U.S.A.). *Anal. Chem.*, 33 (1961) 325.
The quantity of electricity consumed in a cathodic stripping process after the pre-electrolysis step which causes a deposition of silver halide, is used for the determination of iodide in solutions as dilute as $4 \cdot 10^{-8}$ M. The silver-iodide is deposited on an electrode with an area of approximately 0.06 sq.cm. The silver-iodide is then stripped by electrolysis at constant or linearly varying tension. In the first case the stripping time is limited to 15 sec and the current time curve integrated.

In the second case the surface under the peak is used for determining the iodide. The average deviation is between 0.9 and 4% or 0.6 and 2.5% respectively in a concentration range from 10^{-5} to 10^{-8} *M*. The method is also applied to the determination of chloride in 80% ethanol. [Kl.Gr.]

286 – Coulometric determination of uranium in power-reactor-fuel-dissolver solutions. B. B. Hobbs (Oak Ridge Nat. Lab., Tenn., U.S.A.). *Nuclear Sci. Abstr.*, 15 (1961) 517, Abstr. No. 3981. [Red.]

See also abstracts nos. 58, 145.

8. Electrophoresis

287 – Immunoelectrophoresis. Procedure and application to the study of group-specific in sera Jan Hirschfeld (Dept. of Bacteriology. Karolinska Inst., Stockholm 60, Sweden). *Sci. Tools.* 7 (1960) 18–25.
The technique and theory of the method are briefly illustrated and its high resolving power stressed. By using this sensitive method, about 30 proteic components can be shown to be present in human sera; on the basis of the different behaviour of some of these components the following conclusions can be drawn: (i) at least 9 main types of human sera exist; (ii) the variations are caused by two group-specific systems, one of which has been previously demonstrated by starch-gel electrophoresis (haptoglobin system), the second consisting of the so-called group-specific components, the existence of which is only demonstrable by immunoelectrophoresis. [Ca.Cas.]

288 – Une bande de papier électrophorétique. Examen de l'effet du dextrane en solution colloïdale sur le sérum humain (en Anglais). M. Keler-Bacǒka, Z. Pučar et A. Benaš (Clinique pour maladies internes, Faculté de médecine, Institut Ruder Boskovic et Institut de pathophysiologie, Yougoslavie). *Experientia,* 16 (1960) 488.
Une solution colloïdale de dextrane à 6% injectée *in vivo* ou ajoutée *in vitro* au sérum, modifie le lipidogramme de celui-ci. Entre le point de départ et les globulines γ apparaît une nouvelle fraction de lipides désignée DL. Au cours des expériences, il restait un trouble dans le sérum et un changement dans le protéinogramme électrophorétique. [De.Mo.]

289 – Electrophoretic study on agar gel of proteolytic and esterase activity in a rabbit spleen extract (in French). J. Uriel, T. Webb and C. Lapresle (Service de Chimie Microbienne, Institut Pasteur, Paris, France). *Bull. soc. chim. biol.,* 42 (1960) 1285–1291.
Methods for detecting proteolytic and esterase activity in protein mixtures separated by electrophoresis on agar gel have been described. This technique was applied to the study of a rabbit spleen extract. Several protein fractions were shown to have esterase activity and not proteolytic activity. One fraction with proteolytic activity at pH 3.5 was detected and its mobility determined. [Gio.Ser.]

290 – Paper electrophoresis (in Japanese). H. Sugano. *J. Japan. Chemistry,* 14 (1960) 342–349.
A review. (Ed.)

291 – Paper electrophoresis of alkaloids (in French). R. Paris and G. Faugeras (Faculté de Pharmacie, Paris, France). *J. pharm. Belg.,* 14 (1959) 15–21.
Extensive work has been carried out using various conditions, and the following conclusions were drawn: the solvent employed may be the same as that used for extraction etc.; 0.5–10 µg of the base are necessary in a volume of upto 50 µl; spots may be detected by means of u.v., iodine, Dragendorff's reagent (quantitative results being possible by photometry), or preferably with a reagent able to distinguish the M.Wts. (*J. Pharm. Chim.,* 2 (1925) 59). Volatile acids (*e.g.* 2 *N* formic acid) or bases (*e.g.* 10% NH_3) are recommended as buffers; the current should be kept low and the field strength high. [Ca.Cas.]

292 – Direct photometry of proteins (separated by electrophoresis) in far u.v. N. Ressler and S. D. Jocobsen (Wayne County General Hospital, Eloise, Mich., U.S.A.). *J. Lab. Clin. Med.,* 54 (1959) 115–124.
Since the various proteic fractions of human serum have very similar absorption coefficients and

follow Beer's law under the conditions usually encountered in gel electrophoresis, a simple method for direct quantitative photometry has been devised: a Tris-buffer and LiCl-containing electrolyte are placed in layers on a quartz slide, electrophoresis is carried out and then the optical transmissions at 200 mμ of the various fractions are recorded by interposing the slide between a u.v. monochromator and a photographic plate. The results are as good as with the conventional colorimetric method. [Ca.Cas.]

293 – Cathode-ray polarography of 2-pyrrole-aldehyde and its n-methyl derivative (in Italian). F. Cappellina and A. M. Drusiani ('G. Ciamician' Inst., Bologna, Italy). *Ricerca sci.* (Suppl. No. 5, Contributi di Polarografia). 5 (1960) 297–307.
Both 2-pyrrole-aldehyde and 1-methyl-2-pyrrole-aldehyde, when reduced at the dropping mercury electrode, show a sharp peak in the oscillograph obtained by using a single-sweep linear voltage variation. The first compound is reduced with a more negative value of E_p. The variation of peak tensions and peak height with both pH and sweep rate is investigated. Evidence is given that the electrode processes are nearly reversible. [Fr.Pan.]

294 – Application of density-gradient electrophoresis to the separation of serum proteins. K. S. Wiarda, A. J. Hyman and A. A. H. Kassenaar (University Hospital, Leiden, The Netherlands). *Clin. Chim. Acta*, 5 (1960) 289–295.
Different buffers have been used, and the mobilities of different proteins are reported. The results and the conditions for obtaining the best separation are discussed. [Gio.Ser.]

295 – Identification of pholcodine by microelectrophoresis on paper. Differentiation from codeine, codethyline and morphine (in French). A. Roux and J. Roux-Matignon (Pharm. du Centre Hosp. Régional, Grenoble, France). *Ann. pharm. franç.*, 18 (1960) 135–138.
Pholcodine can be separated from codeine, ethylmorphine and morphine by electrophoresis on paper using 1% acetic acid as supporting electrolyte. Draggendorff's reagent is used for the detection of the spots. Electrophoresis carried out in 10% NH_3 can also be used for the separation of morphine although the other compounds are not separated. Syrups may be analysed directly or by preliminary extraction with $CHCl_3$, followed by dissolution of the $CHCl_3$ residue in ethyl alcohol. Pholcodine is extracted from solid preparations or from suppositories with 90% ethanol. [Gio.Ser.]

296 – Recherche sérologique concernant la recherche de la taraxéine (en allemand). H. P. Rieder G. Ritzel, H. Spiegelberg et R. Gnirss (Laboratoire de Neurologie de l'Université, Bâle, Suisse). *Experientia*, 16 (1960) 561.
Dans le cas de malades atteints de schizophrénie aiguë, la taraxéine du sérum ne peut pas être détectée par immunoélectrophorèse, ni par hemagglutination des cellules colorées, ni par le test d'agglutination des particules de latex. [De.Mo.]

297 – Electrophoretic purification of highly active secretion preparations (in English). Viktor Mutt (Chem. Dept. II, Karolinska Institute, Stockholm, Sweden). *Arkiv. Kemi*, 14 (1959) 273–278.
The secretion is purified electrophoretically. 0.1 *M* ammonium bicarbonate, pH 7.6–7.8, which is easily removed on lyophilizing the fractions from the columns, was used as the buffer. The jacketed columns are cooled with cold running tap water. [St.Bre.]

298 – The separation of propioguaiacone from its lower homologues and some related catechol-type phenols using oxy-anions as chelating and buffering agents (in English). Jaakko Halmekoski (Dept. of Chem., University of Helsinki, Finland). *Suomen Kemistilehti*, 33 (1960) B 74–76.
Paper chromatographic and electrophoretic analyses of propioguaiacone in the presence of some other typical phenols obtained from the degradation of lignin have been carried out. Separation of vanillin, acetoguaiacone, propioguaiacone, protocatechuic aldehyde and acetopyrocatechol has been achieved by paper chromatography using chelation reactions between the catechol-type phenols and oxy-anions of some elements in Groups III and VI of the periodic system and immobile aqueous phases with increasing pH-values due to the hydrolysis of the oxy-anions. See also following abstract. [St.Bre.]

299 – The separation of acetopyrocatechol from catechol and some 4-substituted catechol- or guaiacol-type phenols using chelation reactions (in English). Jaakko Halmekoski (Inst. Chem., University of Helsinki, Finland). *Suomen Kemistilehti*, 32 (1959) B 170–172.
The paper chromatographic and electrophoretic identification of acetopyrocatechol in the presence of some other phenols of the types obtained in the degradation of lignin has been carried out. Separation of vanillin, acetoguaiacone, acetopyrocatechol, catechol, protocatechuic aldehyde and protocatechuic acid was achieved with the aid of chelation reactions between the catechol-type

phenols mentioned and oxy-anions of some elements in Groups III and VI of the periodic system. See also preceding abstract. [St.Bre.]

300 – Colorimetric and electrophoretic techniques to determine glutamic acid in the presence of γ-aminobutyric acid, with a reference to the estimation of the storage condition of wheat (in English). Pekko Linko (Kansas State University, Manhattan, Kansas, U.S.A.). *Suomen Kemistilehti*, 33 (1960) B 145–149.
A colorimetric method for the quantitative determination of glutamic acid in the presence of γ aminobutyric acid has been developed. Using both this technique and paper electrophoresis, the glutamine acid decarboxylase activity of wheat was determined and used to estimate the degree of deterioration of stored wheat. [St.Bre.]

301 – Distribution of proteins in electrophoresis on a column of cellulose acetate by the method of Tiselius, Flodin and Porath (in French). J. Enselme, J. Tigaud and J. Frey (Faculté de Médicine et Pharmacie, Lyon, France). *Bull. soc. chim. biol.*, 41 (1959) 1373–1383.
Serum proteins have been separated on a column of cellulose acetate by electrophoresis using the method of Tiselius, Porath and Flodin. The apparatus is described and the method of preparation of the acetylated cellulose given. The cellulose acetate is suspended in barbitone buffer at pH 8.6, with an ionic strength of 0.025. Methods for the identification of the different proteins are given, and the results obtained are compared with those obtained by free electrophoresis. The separation is good but the bands are more diffuse when cellulose acetate is present, so that some overlapping between neighbouring bands occurs. [Gio.Ser.]

302 – Influence of some amino acids on the electrophoretic behaviour of local anaesthetics (in Italian). G. Marras and E. Farine (Inst. Pharm. and Gen. Chem., University of Sassari, Italy). *Boll. soc. ital. biol. sper.*, 36 (1960) 53–55.
The migration of the local anaesthetics, farmocaine, lignocaine, amylocaine, and cinchocaine, under the influence of various amino acids has been studied. Electrophoresis was carried out on Whatman No. 3 MM paper in a buffer of pH 2.1 with a potential gradient of 7 V/cm. The amino acid concentration was in every case four times the concentration of the anaesthetic. Dragendorff's reagent and ninhydrin were used to reveal the spots.
Aspartic acid, tryptophan, cysteine and leucine all reduced the migration of the anaesthetics, while all the other amino acids tested did not. Amylocaine migration was affected by all the amino acids tested. The amino acids were detected in the zone of the retarded anaesthetics. The probable *in vivo* effect of amino acids in annulling the anaesthetic's surface activity may be ascribed to the formation of some kind of complex between the anaesthetic and the amino acid. [Gio.Ser.]

303 – Rapid micro-electrophoresis of serum total proteins and lipoproteins. B. Zak, T. L. Jarkowski and L. A. Williams (Dept. of Pathol., Wayne State Univ. Coll. of Med., Detroit, Mich., U.S.A.). *Am. J. Clin. Pathol.*, 31 (1959) 559–562.
Proteins and lipoproteins in serum can be separated by micro-electrophoresis on dilute agar gel on a tissue slide. A barbitone buffer of 0.05 ionic strength and pH 8.6 is used as the electrolyte, and 175 mg agar per 100 ml of buffer are used as a stabiliser. Amido black is used for the staining of proteins, and oil red O for lipoproteins. [Gio.Ser.]

304 – Albumin–globulin ratio in serum. A comparison of salt fractionation and protein paper electrophoresis. W. B. Yeoman (Frenchay Hospital, Bristol, Great Britain). *Clin. Chem.*, 6 (1960) 122–129.
Paper electrophoresis is used for controlling the efficiency of the separation by precipitation with salt. Analysis of the concentrated filtrate shows that globulins are completely precipitated by 27.2% Na_2SO_4. [Gio.Ser.]

305 – Electrophoresis of nucleic acids in silica gel. D. N. Harris and F. F. Davis (Rutgers University, New Brunswick, N.J., U.S.A.). *Biochem. Biophys. Acta*, 40 (1960) 373–374.
Buffers containing silica gel can be used successfully for the electrophoretic separation of deoxyribonucleic and ribonucleic acids. The silica gel functions as a sieve, the proteins and deoxyribonucleic acid being stopped while ribonucleic acid and peptides migrate. (Gio.Ser.]

306 – Electrophoresis of amino acids on cellulose powder (in French). C. Montant and J. M. Touze-Soulet (Lab. de Cryptogamie, Fac. des Sciences, Toulouse, France). *Bull. soc. chim. biol.*, 42 (1960) 161–166.
With a simple electrophoresis apparatus, the separation of amino acids is possible in quantities up to 40 mg. The electrophoresis is carried out on a cellulose support, using an acetic acid–pyridine–water buffer (10 : 3 : 487) at pH 3.9. The electrophoresis is carried out in a cold room to minimise evaporation, with 250 V applied tension and a current of 80 mA for 14 h. [Gio.Ser.]

307 – Factors affecting albumin trailing during electrophoresis. W. B. Yeoman (Frenchay Hospital, Bristol, Great Britain). *Clin. Chim. Acta*, 5 (1959) 75–81.
The trailing of albumin is affected by a number of factors such as the quality and thickness of the paper, the applied tension and the number of strips run simultaneously. These factors have been studied and are discussed. The trailing on Whatman No. 1 paper at not too large tensions can be estimated to be between 9 and 14% of the albumin present in the serum. A correction method previously used is confirmed. [Gio.Ser.]

308 – Paper electrophoretic determination of hydroxymethylanthraquinone in frangula extracts in the presence of phenolphthalein. M. Sterescu and V. Pelloni (Chem. Pharm. Research Inst., Bucharest, Rumania). *Pharm. Zentralhalle*, 99 (1960) 121–124.
Phenolphthalein is determined in a mixture by submitting an untreated sample to electrophoresis on Whatman No. 1 paper in 0.1 *N* NaOH for 3 h under a tension gradient of 4 V/cm. The appropriate zone is extracted with 0.1 *N* NaOH containing 25% ethanol and the extinction at 530 mμ is measured. The hydroxymethylanthraquinones are determined by refluxing for 1 h a liquid sample of frangula (1 g in 10 ml) with 10 ml $CHCl_3$ containing 1 ml of conc. HCl. After cooling, the $CHCl_3$ is extracted with 0.1 *N* NaOH. The extract is diluted to 25 ml and a 25 μl aliquot is subjected to electrophoresis and absorptiometry as for the phenolphthalein sample. The error is not more than 4%. [Gio.Ser.]

309 – Effects of alternating current overlap and of addition point of sample on the migration and electro-osmosis of acid radicals (in Japanese). Shigeichi Achiwa (Shiga Prefectural University, Shiga, Japan). *J. Electrochem. Soc. Japan*, 27 (1959) 632.
As part of an investigation of the electrochromatographic migration of acid radicals, experiments were carried out to test the effect of superimposed a.c. voltage and of different addition points of the sample on migration and electro-osmosis. The migration of $Fe(CN)_6^{4-}$ (developing solution: 0.04 *M* CH_3COONH_4) on a filter paper immersed in a monochlorobenzene bath was investigated using various applied voltage ratios (d.c./a.c. from 200 V/0 V to 200 V/400 V) and by adding the sample at various points on the filter paper. The movement due to the natural diffusion and electro-osmosis of the developing liquid was measured by adding H_2O_2 solution as a test sample. The migration distance decreased considerably with increase of the distance between the adding point of the sample and the cathode. On the other hand, it increased with increase of the applied a.c. voltage. This phenomenon was interpreted as due to the effects of a.c. overlap and the addition point of the sample on the true electro-osmotic flow and natural diffusion of the developing liquid. [Ta.Fu.]

310 – Paper electrophoretic study of rates of consecutive reactions. The deamidation of vitamin B_{12}. Grant H. Barlow (Abbott Laboratories, North Chicago, Ill., U.S.A.). *J. Chem. Ed.*, 38 (1961) 37.
The progress of the deamidation of vitamin B_{12} to produce carboxylic acids was followed by paper electrophoresis. 20-μl samples were examined periodically using a phosphate buffer of pH 6.2 and ionic strength 0.05 as an electrolyte. A tension of 7 V/cm was applied for 5 h. [D.S.Ru]

311 – Error sources in the determination of glycoproteins of serum by paper electrophoresis (in German). W. Boguth and H. Schnappauf (Chem.-Physiolog. Abt., Veterinär-Physiolog. Institut, Univ. Giessen, Deutschland). *Naturwissenschaften*, 46 (1959) 145–146.
Bei ungenügender Fixierung kommt es zu Albuminverlusten in sauren alkoholischen Reagenzlösungen. Ausserdem führt die Verwendung gebräuchlicher Transparenzöle ($n_D = 1.51$) zu Fehlern, da trockene Proteine etwa den gleichen Brechungsindex $n_D = 1.557$ wie Cellulose haben. Dadurch erscheint der Eiweissfleck zu transparent und die Exstinktion wird bei Auswertung der Papierstreifen zu niedrig gemessen. Optimal ist Transparentflüssigkeit mit $n_D = 1.55$. [H.W.Nür.]

312 – Untersuchungen vom Jensensarkom-Extrakten mittels Endgruppen-Bestimmungen und Papier-Elektrophorese. Hans von Euler, Hans Hasselquist und Hanspetter Erret (Institut für organ. chem. Forschung, Universität, Stockholm, Sweden). *Arkiv Kemi*, 16 (1961) 327–332.
Hinsichtlich des Gehaltes an einzelnen Aminosäuren sind bisher nur relativ geringe Unterschiede zwischen normalen Proteinen verschiedener Organe und der Jensensarkom-Impftumoren nachgewiesen worden (Diazani, DiBella u.a.) und es liegt nahe, die zwischen den durch Mutation entstandenen Tumoren und den normalen Proteinen des gleichen Organismus bestehenden Unterschiede auf die verschiedenen Reihenfolgen der Aminosäuren zurückzuführen. Die ausserordentlich bedeutungsvolle Sequenz der Aminosäuren ist bisher an eine Reihe wichtiger Proteine festgestellt (A. Sanger u.a.), aber über die Anordnung der Aminosäuren in Tumoren und besonders über der Mechanismus, durch welchen (bei der Mutation oder durch Noxen verschiedener Art) doe Sequenz verändert wird, liegen noch ungenügend Anhaltpunkte vor. Wir haben uns aus diesem Grund den Endgruppen-Bestimmungen zugewandt. [Sv.Li.]

313 – Microseparation of tetrazolium salts by paper electrophoresis. M. D. Glantz and F. Fried (Dept. of Chem., Brooklyn College, Brooklyn, New York, U.S.A.). *Microchem. J.*, 3 (1959) 214–216.
Paper electrophoresis has been used for the separation of several tetrazolium salts. Whatman No. 3 MM paper has been used with borate–phosphate buffer at pH 8 and 9. At this pH good separation is achieved in 3 h with a potential gradient of 12 V/cm. The compounds are detected by the formation of coloured compounds, which occurs spontaneously during the drying of the paper, and they can also be detected by ultraviolet scanning. [Gio.Ser.]

314 – Analysis of casein fractions by zone electrophoresis in concentrated urea. R. G. Wake and R. L. Baldwin (Dept. of Biochem., Stanford University, Palo Alto, Calif., U.S.A.). *Biochim. Biophys. Acta*, 47 (1961) 225–239.
Starch-gel electrophoresis of casein in the presence of concentrated urea shows a number of different bands. The number and position of the bands do not depend on the method of preparation, nor on the cow from which the milk was obtained. The different components appear homogeneous when subjected to further electrophoresis in the presence of urea. Details of the technique are given so that the experiments may be repeated under essentially the same conditions. The different components have been studied and compared to fractions obtained by other authors using different methods. An alternative system of nomenclature for the different casein fractions differing from the one commonly adopted is proposed. [Gio.Ser.]

315 – Zone electrophoresis of casein in urea–buffer mixtures. T. A. J. Payens (Netherlands Institute for Dairy Research, Ede, The Netherlands). *Biochim. Biophys. Acta*, 46 (1961) 441–451.
A comparison has been made of the results obtained when casein is subjected to electrophoresis in the presence and absence of urea. The addition of urea at increasing concentrations from 7.5 to 45% improves the separation of casein into two bands, the best results being obtained at a concentration of 30% or 4.6 *M*. The electrophoresis has been carried out in barbiturate buffers at pH 7.5 on Whatman No. 1 paper and at a field strength of 3 V/cm.
By carrying out electrophoresis on cellulose columns three components can be separated: α, β, and k.
The physico-chemical properties, and the sensitivity towards Ca^{2+} ions, and towards the milk-clotting enzyme, rennin, of the different fractions have been studied. The results obtained are discussed and compared with those of other authors obtained by different techniques. [Gio.Ser.]

316 – Electrophoretic comparison of nuclear and nucleolar proteins. I. Beef pancreas C. Poort (Dept. of Hystology, Faculty of Medicine, University of Utrecht, The Netherlands). *Biochim. Biophys. Acta*, 46 (1961) 373.
Paper and agar electrophoresis have been applied to the study of the extracts obtained by different methods from nuclei and nucleoli isolated from beef pancreas.
By comparing the electropherograms, it was shown that the proteins of the nucleoli differ greatly from those of the non-nucleolar part of the nucleus. [Gio.Ser.]

317 – Electrophoresis of proteins from homogenized milk. J. Tobias and R. M. Serf (University of Urbana, Ill., U.S.A.). *J. Dairy Sci.*, 42 (1959) 550–552.
The homogenized milk is diluted 2.5 : 1 with a 0.1 *M* NaCl solution, after which it is dialysed for 30 min at 0—4° *vs.* a 0.1 *M* NaCl solution and centrifuged for 30 min at 37° and 20,000 rev/min. The fat remains in the upper layer and must be carefully taken out to avoid a possible new emulsion. After the fat has been removed it is possible to carry out the electrophoresis of the proteic part of the milk. [G.de An.]

318 – Electro-chromatography in the study of ions. III. H. G. Mukerjee (Scottish Church College, Calcutta-6, India). *Z. anal. Chem.*, 167 (1959) 182–184.
The possibility that nickel ions can migrate as a compact zone in 0.5 *M* tartaric acid, 120 V being applied to the paper strips for 5h, is of great importance for the quantitative separation of these ions and their colorimetric determination; after the nickel band has been revealed on the paper it is cut out, the paper ignited and the metal oxide dissolved. The result indicates that there is no trailing of the band. [G.de An.]

319 – Deposition of carrier-free radioactive isotopes by an electro-chromatographical method (in German). I. Mádi (Institut f. physikal. Chemie, Kossuth-Universität, Debrecen, Ungarn). *Naturwissenschaften*, 48 (1961) 155–156.
Eine Platinpulverkolonne (5 cm Durchmesser, 15 cm lang) dient als Kathode und eine Pt-Nadel als Anode. Die abgeschiedenen radioaktiven isotope werden selektiv eluiert und man erhält so chemisch und radioaktiv reinste trägerfreie Präparate. Bein Atomarten, die sich anodisch als Oxyde abscheiden wird die Pt-Kolonne als Anode geschaltet. [H.W.Nür.]

320 – The detection of adrenaline and arterenole (in German). W. Gross and E. Ambs (Medizin. Poli-Klinik u. Kinderklinik, Univ. Würzburg, Deutschland). *Naturwissenschaften*, 47 (1960) 179.
The separation of both substances was performed in 4 h by paper electrophoresis at high voltages (paper was Macherey and Nagel No. 214, 34 × 18 cm; pH=7.2 with 100 ml pyridine and 900 ml 0.2 *M* CH_3COONa in pure acetic acid; 750 V; 30 mA). The pure substances had a high migration velocity in the anodic direction (11 and 11.5 cm respectively in 4 h), while the extracts from urine (in acetic acid) gave two bands which migrated only 1.5 and 2 cm respectively in the same time. This simple method may be suitable as a separation technique for quantitative analysis. [H.W.Nür.]

321 – Paper electrophoretic identification of microquantities of some toxicologically significant alkaloids and comparison with chromatography. C. Buff, J. Orantes and P. L. Kirk (School of Criminology, University of California, Berkeley, Calif., U.S.A.). *Microchem. J.*, 3 (1959) 13–18.
The procedure is described for the separation of several alkaloids by paper electrophoresis. Nine alkaloids were subjected to electrophoresis at pH 3, 5, 6.5 and 7.5. These were codeine, atropine, morphine, emetine, strychnine, cocaine, heroine, quinine and yohimbine. Tables are included which show that all the alkaloids tested are distinguishable at one or more of the pHs used. The results are compared with the separation of the same alkaloids by paper chromatography. The comparative experiments showed that the mobilities were more easily reproduced than the R_F's, and that separation by electrophoresis was much shorter than by the chromatographic method. [Gio.Ser.]

322 – Paper ionophoresis of glucopyranosyl-fructoses and other substituted fructoses. E. J. Bourne, D. H. Hutson and H. Weigel (Chem. Dept., Royal Holloway College, University of London, Englefield Green, Surrey, Gt. Britain). *Chemistry and Industry*, (1960) 1111.
The migration rates of D-fructose, 1-O-β-D-glucopyranosyl-D-fructose, sucrose, turanose, maltulose, leucrose and isomaltulose have been determined in four electrolytes. The migration rates in borate, molybdate, arsenite and sodium hydroxide solutions indicate that the glucopyranosylfructoses can clearly be distinguished from each other. [D.S.Ru.]

See also abstracts nos. 39, 40, 41, 46, 48, 49, 50, 54, 55, 56, 59, 63, 67, 68, 76.

9. Other methods

323 – Chronopotentiometric studies on the oxidation of ferrocene, ruthenocene, osmocene, and some of their derivatives. Theodore Kuwana, Donald E. Bublitz and George Hoh (Dept. of Chem., University of Kansas, Lawrence, Kansas, U.S.A.). *J. Am. Chem. Soc.*, 82 (1960) 5811–5817.
The chronopotentiometric behavior of ferrocene(I), ruthenocene(II), osmocene(III) and several derivatives of these cyclopentadienyl compounds has been examined at a platinum electrode in acetonitrile solvent. Comparison of the chronopotentiometric constant, $i_0\tau^{1/2}/C$, for I, II and III showed that I gives a one-electron transfer, II a one-step, two-electron transfer, and III a two-step, one-electron each transfer. Values of $E_{1/4}$ for I, II and III are 0.307, 0.693, and 0.633 and 1.50 V *vs.* S.C.E., respectively. The variation of $E_{1/4}$ among the derivatives of I, II and III was in accord with the expected inductive effect of the substituent group and was successfully correlated with the Ingold–Taft equation. $E_{0.22}$ data from current reversal chronopotentiograms indicated that I and its derivatives undergo reversible electrode reactions, while II and III are irreversible. [Roy.Mur.]

324 – Influence of dielectric constant and added electrolyte on the ion pair formation of dimethylaminoazobenzene in acetic acid–acetic anhydride mixtures (in English). Jouko Kenttämaa, Pentti Järvi and J. Johan Lindberg (Inst. of Chem., University of Helsinki, Finland). *Suomen Kemistilehti*, 33 (1960) B 101–104.
A change in the dielectric constant does not seem to have any influence on the molecule–ion pair equilibrium of dimethylaminoazobenzene (butter yellow) in acetic acid–acetic anhydride mixtures. The addition of sodium acetate slightly favours the ion pair formation in pure acetic acid but the effect is the opposite in mixtures containing acetic anhydride. pK_d for the ion pair–free ion equilibrium seems to vary linearly with 1/D in the usual way. [St.Bred.]

325 – Some considerations of the structures of dimethyl sulphoxide–water mixtures in the light of thermodynamic and dielectric behaviour (in English). J. Johan Lindberg and Jouko Kenttämaa (Inst. of Chem., University of Helsinki, Finland). *Suomen Kemistilehti*, 33 (1960) B 104–107.
The structures of dimethyl sulphoxide–water mixtures are discussed in the light of thermodynamic excess functions and dielectric data. It seems that a classification of binary aqueous nonelectrolyte mixtures can be based on dielectric excess functions. The dielectric constants of dimethyl sulphoxide–water mixtures were determined at 2.47 Mc and 25° by the resonance method. [St.Bred.]

326 – Dielectric constants of acetone–dioxan and acetone–tetrahydrofuran mixtures (in English). J. Johan Lindberg (Inst. of Chem., University of Helsinki, Finland). *Suomen Kemistilehti*, 32 (1959) B 12–14.
The dielectric constants of acetone–dioxan and acetone–tetrahydrofuran mixtures have been determined at 25° by the heterodyne beat method employing a frequency of 500 kc. [St.Bred.]

327 – Dielectric determination of moisture in substances insoluble in dioxane. Application to sucrose and to refined sugar (in Italian). L. Cavallaro and L. Felloni (Chem. Inst., University of Ferrara, Italy). *Industria saccar. ital.*, 52 (1959) 57–67.
Methods for the determination of moisture are reviewed. A method is described based on the measurement of the dielectric constant of 1,4-dioxane. The measurement of the capacity of electric condensers is carried out at 25° ± 0.02°, and at a frequency of 1 MHz. The 1,4-dioxane must be purified and any trace of moisture must be avoided. The dielectric constant varies linearly with the water content of the mixture. The 1,4-dioxane is used with sucrose and refined sugars since it is completely miscible with water and does not dissolve sucrose. Commercial dioxane can also be used, but the results are not so good. Results for refined sugar are in agreement with those obtained by the drying method, with an accuracy of 0.01%. The whole analysis may be completed in less than 30 min. [Gio.Ser.]

328 – Analysis of technical formaldehyde solutions (in German). F. Oehme (Inst. for Development of Modern Phys. Chem. Anal. Methods, Weilheim/Obb., Germany). *Kunststoffe*, 49 (1959) 226–227.
A triangular diagram is reported, from which the amounts of components present in technical formaldehyde–methanol solutions can be calculated when the dielectric constant and specific gravity are known; in the absence of methanol, knowledge of only the first parameter is needed. [Ca.Cas.]

329 – Chronopotentiometry at the dropping mercury electrode. Especially the use of the slow dropping mercury electrode (SDME) (in Japanese). Masayoshi Ishibashi, Taitiro Fujinaga, Atsuyoshi Saito and Kosuke Izutsu (Chem. Inst., Faculty of Science, Kyoto University, Japan). *J. Electrochem. Soc. Japan*, 27 (1959) 98–100.
The electrical tension–time relationship of the DME under controlled current electrolysis was investigated theoretically. It was shown that the measurement of electrical tension–time curves is promising for analytical purposes, especially for the determination of trace elements in the presence of large amounts of more positively reducible substances. This technique (chronopotentiometry at the DME) was applied to the trace analysis of Cd in the presence of large amounts of Pb. The slow dropping mercury electrode was used instead of a conventional DME. Cd in the range $1\cdot10^{-3} \sim 2\cdot10^{-5}$ M can be determined in the presence of 10^{-3} M Pb in 0.5 M HCl. $2\cdot10^{-6}$ M Cd in the presence of 10^{-4} M Pb can also be determined. [Ta.Fu.]

330 – The dielectric properties of water in dioxane. A. R. Tourky, H. A. Rizk and Y. M. Girgis (The National Research Centre, Cairo, Egypt). *J. Phys. Chem.*, 65 (1961) 40–42.
The apparent solution moment of water in dioxane is 1.093 ± 0.03 D. The electrical anisotropy of water above 83 mol.% approaches that of pure water. The coordination number in liquid water appears to be about 6, which would yield the value 1.86 D for the vapor moment by Kirkwood's equation. In a solution containing 83 mol.% water, the relaxation time is about double that of pure water, and in 60 mol.% the enthalpy of activation for viscous flow is nearly equal to that of pure water. [D.S.Ru.]

331 – Microwave absorption and molecular structure in liquids. XXXV. Absorption by pure polar liquids at 4.3 mm wave length. Worth E. Vaughan and Charles P. Smyth (Frick Chem. Lab., Princeton University, New Jersey, U.S.A.). *J. Phys. Chem.*, 65 (1961) 98.
The dielectric constants and losses of chlorobenzene, tribromofluoromethane, phenyl ether,

benzophenone, anisole, *o*-dimethoxybenzene, *m*-dimethoxybenzene and *p*-dimethoxybenzene have been measured at 4.35 mm wave length between 20 and 80°. A second dispersion region has been found for benzophenone which may be explained in terms of an intramolecular mechanism. Intramolecular rotation also has been found in the molecules of the four aromatic methoxy compounds. [D.S.Ru.]

332 – The complex dielectric constants of solutions of trimethylpentane and nitrobenzene near the consolute temperature. B. D. Ripley and R. McIntosh (Dept. of Chem., University of Toronto, Canada). *Can. J. Chem.*, 39 (1961) 526–534.
The complex dielectric constants of three compositions of trimethylpentane and nitrobenzene have been measured as a function of temperature for a range near the consolute temperature. The chemical systems showed maxima in both the real and imaginary parts of the complex dielectric constant at temperatures above those at which phase separation occurs. A discussion of the validity of applying thermodynamic formulae to dielectrics showing loss is given and some qualitative remarks are offered concerning the change of the systems as they are cooled. [D.S.Ru.]

333 – Dielectric relaxation in liquids. I. The representation of relaxation behavior. B. W. Davidson (Applied Chem. Div., National Research Council, Ottawa, Canada). *Can. J. Chem.*, 39 (1961) 571–594.
Methods are described for the determination of the parameters used in the skewed-arc representation in the complex dielectric constant plane of dielectric relaxation in liquids. Graphs give the frequency dependence of the real and imaginary parts of the dielectric constant predicted by the skewed-arc equation. Evidence is presented for the frequent occurrence of this type of relaxation behavior in liquids.
It is concluded that skewed-arc characteristics arise from the presence of co-operative relaxation processes, possibly aided by the diffusion of disordered regions, in which the individual mechanisms of relaxation cannot be resolved by application of the superposition principle. [D.S.Ru.]

334 – Ion exchangers as high-molecular polyelectrolytes (in German). N. A. Ismailow (Chem. Institut, Universität Charkow, U.S.S.R.). *Z. physik. Chem. (Leipzig)*, 215 (1960) 314–339.
Ion exchangers may be treated theoretically as high-molecular polyelectrolytes. Ion exchange equilibrium is dependent on the properties of the ion exchanger, the exchanged ions and nature of the medium. The high-molecular polyelectrolytes react, depending upon the medium, as acids, bases or salts and they may be strong or weak electrolytes. Therefore the selectivity may be controlled by the use of suitable solvents. Dissociation is only possible if one ion is changed into another one and adsorption phenomena are superposed on electrochemical effects. Therefore the ion exchange constants for which a general equation is derived are really not constant. [H.W.Nür.]

335 – The temperature and counter-ion dependency of cation exchange equilibria (in English) O. D. Bonner, G. Dickel and H. Brümmer (Phys. Chem. Inst., University of München, Germany and Dept. of Chem., University of South Carolina, Columbia, S.C., U.S.A.). *Z. physik. Chem. (Frankfurt)*, 25 (1960) 81–89.
For four systems (nitrates and chlorides of Ca,Mg,Cu) ion exchange equilibria at 0°, 25°, 54°, 75° and 98.5° in solutions of 0.1 ionic strength have been determined. Evidence of a $CuCl^+$-complex is observed, the stability of which increases with temperature. Donnan uptake measurements confirm these observations. The activity coefficients of $CaCl_2$ and $Ca(NO_3)_2$ show anomalies between 50° and 75°. The values of $\Delta F°$, $\Delta H°$ and $\Delta S°$ are calculated for the exchange systems. [H.W.Nür.]

336 – Variations in the structure of sulfonic acid type cation exchanger resins and the effect of these variations on their properties. O. D. Bonner and R. R. Pruett (Dept. of Chem., University of South Carolina, Columbia, S.C., U.S.A.). *Z. physik. Chem.* (*Frankfurt*), 25 (1960) 75–80.
The relationship between water uptake, divinylbenzene content, extent of sulfonation and resin selectivity is discussed for sulfonated styrene-divinylbenzene-type exchangers (DOWEX). [H.W.Nür.]

337 – Studies on ion exchange equilibrium of the sodium isotopes on cation exchange resins. II. Sodium chloride in dioxane–water mixtures. H. Ohtaki (Chem. Inst. Faculty of Science, Nagoya University, Japan). *Z. physik. Chem. (Frankfurt)*, 27 (1961) 209–220.
The selectivity coefficients between Na-23 and Na-24 on differently cross-linked Dowex-50 resins (sulfonated styrene-divinylbenzene-type) and on phenolsulfonic acid resin are determined. After attaining equilibrium the resin was separated from the solution, the adsorbed solvent washed out with methanol and the amount of water in the washings titrated with Karl-Fischer

reagent, while the amount of adsorbed dioxane was obtained from the difference of the total amount of mixture adsorbed (determined by radioactivity) and the titrated water. The higher the degree of cross-linkage, the smaller the volume adsorbed. On highly cross-linked resins water is adsorbed more selectively from the mixtures. The higher the NaCl concentration, the less the percentage of adsorbed water. The selectivity coefficients for Na-isotopes were not appreciably different with Dowex-50 from those obtained in ethanol–water. A very important factor of the same degree as cross-linkage and concentration are the dielectric constants in solution and on the resin. [H.W.Nür.]

338 – Electrolytic transition of Ag_2O to AgO in alkaline solutions. Thedford P. Dirkse and George J. Werkema (Dept. of Chem., Calvin College, Grand Rapids, Mich., U.S.A.). *J. Electrochem. Soc.*, 106 (1959) 88–90.
The electrolytic oxidation of silver in alkaline solution was studied by an interrupted current technique. Special attention was given to a short tension maximum preceding the tension-level corresponding to the formation of AgO. This maximum in the tension–time curves was interpreted as being due to the high electrical resistance of the Ag_2O layer, rather than to the transient existence of Ag_2O_3. [Fe.Jol.]

339 – Phthalocyanines as oxidation–reduction indicators. V. Titration of iron(II), uranium(IV) and molybdenum(V) with sodium vanadate. G. Gopala Rao and T. P. Sastri (Dept. of Chem., Andhra University, Waltair, India). *Z. anal. Chem.*, 167 (1959) 1–8.
The use of a 0.1% solution of copper phthalocyanine tetrasulphonic acid (see also *Z. anal. Chem.*, 163 (1958) 266) in 50—60 ml solution as an oxidation–reduction indicator in vanadimetry is discussed and related to the nature and concentration of the acid present (H_2SO_4,HCl,H_3PO_4,H_2CrO_4). The colour change is green (red.) to pink (ox.).
Titration of iron(II) with 0.05 *N* sodium vanadate solution and 3 drops/60 ml of indicator can be performed in 12 *N* H_2SO_4 + 3 ml/60 ml H_3PO_4, or in 14 *N* H_2SO_4 alone, without indicator correction. For less iron content and using 0.01 *N* sodium vanadate, titration can be performed in 12 *N* H_2SO_4 without H_3PO_4 and the indicator correction is 0.02 ml, which is smaller than those needed when diphenylbenzidine or N-phenylanthranilic acid are used. The error is less than 1%. The iron titration is not possible in HCl medium. The determination of uranium(IV) and molybdenum(V) is carried out in 12 *N* H_2SO_4 + 3 ml/60 ml H_3PO_4; 14 *N* (or more) H_2SO_4 is deleterious. The error is less than 1%. [G.de An.]

340 – Rapid dielectric determination of residual water content in inorganic fertilizers (in German). F. Oehme (Institut zur Entwicklung chemisch-physicalischer Analysenmethoden, Weilheim/Obb., Deutschland). *Z. anal. Chem.*, 167 (1959) 271–277.
A new method is described for determining the residual water content ($<3\%$) of inorganic fertilizers in about 3 min. The method is based on the determination of the dielectric constant of powdered salts by an immersion procedure, using benzene as the liquid phase. The apparatus and the procedure for the calibration and the determination are described in detail with two examples. [G.deAn.]

341 – Investigation of ion exchange at glass electrodes by radioactive isotopes in alkali solutions (in German). K. Schwabe and H. Dahms (Zentralinstitut f. Kernforschung, Rossendorf b. Dresden, Deutschland). *Naturwissenschaften*, 47 (1960) 351–352.
In stark alkalischen Lösungen findet nicht nur ein Na^+-Austausch zwischen den beiden Phasen statt, sondern H^+-Ionen im Glas werden gegen Na^+-Ionen in der Lösung ausgetauscht. Die Zeitabhängigkeit der Na-Aufnahme bzw.-Abgabe wurde mit dem Zählrohr in Na^+-24 markierten Lösungen bzw. an Na^+-24 markierten Glasfolien verfolgt. Während das Erreichen der Na^+-Gleichgewichtskonzentration in der gesamten Quellschicht Stunden erfordert, stellt sich das spannungbestimmende Gleichgewicht an der Phasengrenze sehr schnell ein, so dass der bekannte Alkalifehler der Glaselektrode in stark alkalischer Lösung praktisch sofort nach Eintauchen auftritt. Der H^+-Gehalt der Quellschicht folgt aus Tritiummessungen. [H.W.Nür.]

342 – The dielectric properties of tetra-*n*-butylammonium picrate, bromide and tetraphenylboride in some polar solvents at 25°. W. R. Gilkerson and K. K. Srivastava (Dept. of Chem., University of South Carolina, Columbia, S.C., U.S.A.). *J. Phys. Chem.*, 65 (1961) 272–274.
The dielectric constants of solutions of tetra-*n*-butylammonium picrate in *o*-dichlorobenzene–benzene solvent mixtures, chlorobenzene and in bromobenzene, of tetra-*n*-butylammonium bromide in chlorobenzene and bromobenzene and of tetra-*n*-butylammonium tetraphenylboride in chlorobenzene have been determined at 1 Mc at 25°. Dipole moments for the ion pairs were calculated using Onsager's equation. The results have been interpreted in terms of polarization of the ions to yield smaller moments. [D.S.Ru.]

343 – EDTA as a micro-analytical reagent. A. J. Barnard, Jr., W. C. Broad and H. Flashka (J. T. Baker Chem. Co., Philipsburg, New Jersey, and Dept. of Chem., Georgia Inst. of Technol., Atlanta, Ga., U.S.A. *Microchem. J.*, 3 (1959) 43–64.
A review of the applications of EDTA as a reagent in micro-analysis. 196 references. [Gio.Ser.]

See also abstracts nos. 32, 35, 42, 64, 65, 120.

10. Related topics

344 – A note on the paper of A. MITUYA and T. OBAYASHI "The deterioration of platinum anodes in acid solutions". A. N. Frumkin (Inst. of Electrochem., Academy of Sciences, Moscow, U.S.S.R., *J. Research Inst. Catalysis, Hokkaido Univ.*, 8 (1960) 10.
A discussion of previous papers by Mituya (*J. Research Inst. Catalysis, Hokkaido Univ.*, 4 (1956) 228; *J. Phys. Chem. U.S.S.R.*, 34 (1960) page not specified), concerning the theory of hydrogen overvoltage on mercury; considering the peculiar technique used by the Japanese author and the very evident discrepancy between the experimental data found by him and the data obtained by Russian workers, it is suggested that some sources of error may have been overlooked by Mituya. [Ca.Cas.]

345 – Oscillographic study of the kinetics of electrode processes. II. The cobalt electrode in cobalt sulphate solutions (in Russian). V. A. Zinovev, A. B. Sheinin and V. L. Kheifetz (State Inst. for the Nickel, Cobalt and Lead Industries, U.S.S.R.). *Zhur. Fiz. Khim.*, 35 (1961) 98–101.
On the basis of oscillographic measurements it has been shown that the kinetics of discharge and ionization of cobalt in cobalt sulphate solutions obey the slow discharge theory. From oscillograms of the breaking of the anodic polarization current, values were determined for the exchange current of cobalt and for the α-coefficient in cobalt sulphate solutions of various concentrations. The coefficient is independent of the concentration and is equal to 0.65. The standard value of the exchange current of cobalt is $3 \cdot 10^{-5}$ A/cm^2. The logarithm of the exchange current of cobalt is a linear function of the logarithmic activity of its ions in solution, with a slope equal to $1\text{-}\alpha$. [Ot.So.]

346 – Cathodic polarization during the simultaneous cathodic discharge of iron, cobalt and hydrogen ions and the reduction of Fe^{3+} to Fe^{2+} (in Russian). A. L. Rotinyan and E. N. Molotkova (Inst. of Technol., Leningrad, U.S.S.R.). *Zhur. Fiz. Khim.*, 35 (1961) 158–163.
The cathodic polarization during the simultaneous deposition of iron and cobalt and the reduction of Fe^{3+} to Fe^{2+} has been investigated at different temperatures. For solutions of cobalt and iron sulphates with pH values 3.5, 1.8 and 1.5, depolarization of the iron and superpolarization of the cobalt take place as well as formation of alloys at the cathode.
Deposition of the alloys at all the temperatures investigated became more difficult with increasing hydrogen ion concentration. The activation energy of the discharge of hydrogen ions and the exchange current for the cobalt–iron alloy were calculated. The more acid the solution, the more prominent became the Fe^{3+} ion formation in the solution and the intermediate reduction of Fe^{3+} to Fe^{2+} at the cathode. All the data fit satisfactorily into the framework of the slow ion discharge theory. [Ot.So.]

347 – Electrochemical and photoelectrochemical behaviour of the silicon electrode (in Russian). S. U. Izidinov, T. I. Borisova and V. I. Veselovskii (L. J. Karpov' Inst. of Phys. Chem., U.S.S.R.). *Doklady Akad. Nauk S.S.S.R.*, 133 (1960) 392–395.
The dissolution of *n*- and *p*-type silicon monocrystals in 0.01–10 *N* KOH solutions was investigated. Curves showing the dependence of the electric tension on time for silicon samples with various types of surface were given for the cases of the sample being immersed in KOH solution and of anodic polarisation. The photogalvanic activity of the samples was found to be dependent on the surface treatment. The non-dependence of the rate of solution on the type of conductivity was found to be conditioned by a pair of conjugated reactions, oxidation and reduction, taking place simultaneously on the silicon surface. [Ot.So.]

348 – Excess free energy in dehydrogenated palladium. J. M. Singer and G. W. Castellan (Dept.

of Chem., The Catholic University of America, Washington 17, D.C., U.S.A.). *J. Chem. Phys.*, 33 (1960) 633–634.
The Authors have measured the electrical tension of the palladium–palladous ion couple in hydrochloric acid solutions using palladium subjected to different treatments.
The palladium pieces alloyed with hydrogen and dehydrogenated using ceric sulfate solution were less noble than those which were not alloyed with hydrogen. The tensions were 0.726 V (*vs.* S.C.E.) for "untreated" Pd and 0.707 V for gas-charged Pd or electrolytically charged Pd. This indicates that a distortion free energy of about 900 cal/mol remains in the metal after the hydrogenation–dehydrogenation cycle. [G.Mar.]

349 – Anodic oxidation of rhenium (in Russian). V. A. Lavrenko (Institute of Special Alloys, Academy of Sciences, U.S.S.R.). *Zhur. Fiz. Khim.*, 35 (1961) 198-200.
The anodic behaviour of rhenium in the recrystallized and cold worked states was studied in 30% H_2SO_4 by the polarisation and charging curve methods. The activation energy of the oxidation reaction depends upon the state of the system at the metal–oxide boundary. Cold working increases the number of active reaction centres, facilitating the oxidation process and the subsequent dissolution of the higher rhenium oxides. [Ot.So.]

350 – Formation and growth of pitting corrosion on passivated iron electrodes (in German). G. Herbsleb and H. J. Engell (Max-Planck-Institut f. Eisenforschung, Düsseldorf, Deutschland). *Z. physik. Chem. (Leipzig)*, 215 (1960) 167–175.
Passivierte Eisenelektroden wurden bei potentiostatisch kontrollierten Spannungen des Passivbereiches in 1 *N* H_2SO_4 der aktivierenden Einwirkung von Cl^--Ionen ($7 \cdot 10^{-4}$ bis $1 \cdot 10^{-2}$ Mol/liter) ausgesetzt und ihre Oberfläche gefilmt. Das Zeitgesetz der Lochbildung (linear) und das Wachstumsgesetz der Löcher (unabhängig vom Elektrodenpotential, Lochgrösse und Versuchsdauer) konnten ermittelt werden. Die Lochzahl hängt von der Elektrodenvorbehandlung ab (Präformierung der Lochkieme). In den Löchern liegt Widerstandspolarisation vor, wahrscheinlich durch $FeSo_4$-Ausfällung. Nach einiger Zeit repassivieren sich die Löcher aus bisher ungeklärten Gründen und wachsen nicht weiter. [H.W.Nür.]

351 – Influence of alloy components on electrochemical behaviour of stainless steel (in German). H. J. Engell and T. Ramchandran (Max-Planck Institut f. Eisenforschung, Düsseldorf, und Versuchsanstalt d. Bergischen Stahlindustrie, Remscheid, Deutschland). *Z. physik. Chem. (Leipzig)*, 215 (1960) 176–184.
Stahl passiviert sich in gegebener Lösung, wenn seine Passivierungsstromdichte I_p kleiner als die Reduktionsstromdichte I_r der reduzierbaren Bestandteile der Lösung beim Passivierungsspannung E_p ist. Je kleiner I_p und je unedler E_p ist, desto leichter tritt Passivierung ein. Die passive Auflösungsstromdichte I_k charakterisiert ausserdem das Korrosionsverhalten. Potentiostatisch registrierte stationäre Stromdichte–Spannungs-Kurven einer Reihe legierter Stähle wurden in H_2SO_4 bei verscheidenen Temperaturen aufgenommen und die so erhalteten charakteristischen elektrochemischen Daten der Stähle tabelliert. Ni-, Cu- und Mo-Zusätze begünstigen die Beständigkeit des passiven Zustandes und erleichtern die Passivierbarkeit durch Herabsetzung von I_p und I_k. In gleicher Richtung wirkt eine Steigerung des Cr-Gehaltes, jedoch vorwiegend durch Negativierung von E_p. [H.W.Nür.]

352 – The behavior of platinum electrodes. Atusi Mituya and Takeko Obayashi (Dept. of Chem., St. Paul's University (Rikkyo Daigaku), Tokyo, Japan). *J. Research Inst. Catalysis, Hokkaido Univ.*, 8 (1960) 79.
It is experimentally shown by using neutron irradiated Pt that the metal dissolves in acid solution after appreciable (more than 1 V) anodic polarization in air. From quantitative measurements it follows that the hypothesis advanced by Frumkin (disintegration of an oxide film formed during previous exposure to air) must be discarded, and the cause of the discrepancies (*cf. J. Research Inst. Catalysis, Hokkaido Univ.*, 8 (1960) 10) must be sought elsewhere. [Ca.Cas.]

353 – The role of the electrokinetic potential in some surface tension phenomena. Lawrence Baylor Robinson (Space Technology Lab., Inc., Los Angeles, Calif., U.S.A.). *J. Electrochem. Soc.*, 106 (1959) 520–524.
The Wagner–Onsager–Samaras theory predicts an increase in the surface tension of water on the addition of an electrolyte. Precise measurements of the surface tension by the capillary rise method have shown an initial decrease and a minimum in the surface tension–concentration curve. The agreement between theory and experiment can be re-established by introducing electrokinetic effects. [Fe.Jol.]

354 – Mechanisms of hydrogen producing reactions on palladium. VI. Atomic hydrogen overvoltage

on an α-Pd–H bielectrode. Sigmund Schuldiner (U.S. Naval Research Lab., Washington, D.C., U.S.A.). *J. Electrochem. Soc.*, 106 (1959) 440–444.
The electrochemical behaviour of an α-Pd–H bielectrode has been studied under conditions where the only reactions on the cathodic and anodic surfaces are the formation and ionization of atomic hydrogen. The atomic hydrogen overtension on this bielectrode has been obtained. There is agreement between a kinetic analysis of the system and the experimental results. [Fe. Jol.]

355 – The mechanism of blackening of nickel anodes. Thomas C. Franklin and Jack Goodwyn (Chem. Dept., Baylor University, Waco, Texas, U.S.A.). *J. Electrochem. Soc.*, 106 (1959) 269–271.
The mechanism of formation and the composition of the black deposit obtained on nickel anodes in a potassium thiocyanate bath have been studied. The bath was of the following composition: $NiSO_4 \cdot 6\,H_2O$, 70 g/l; $(NH_4)_2SO_4$, 37 g/l; $ZnSO_4 \cdot 7\,H_2O$, 34.3 g/l; and KSCN, 17.9 g/l.
It was concluded that the black deposit was nickel sulfide, obtained by the action of transitory monovalent nickel on the thiocyanate ion, according to the following reactions:

$$Ni \rightarrow Ni^+ + e^-$$
$$2\,Ni^+ + CNS^- \rightarrow NiS + CN^- + Ni^{2+}.$$

[Fe. Jol.]

356 – The potential of the manganese dioxide electrode and the surface composition of the oxide. Akiya Kozawa (Dept. of Chem., Western Reserve University, Cleveland, Ohio, U.S.A.). *J. Electrochem. Soc.*, 106 (1959) 79–82.
On heating different kinds of manganese dioxide at 100–450° their tension, discharge capacity and water content are affected, although their decomposition temperature lies at higher values, between 480 and 580°. The tension decrease on heating can be explained as the result of lower oxide film formation. Reaction of Mn^{2+} in slightly alkaline electrolyte with MnO_2 gives a similar decrease in tension due to surface effects. [Fe. Jol.]

357 – Influence of the state of platinum anodes on the electric tension of the oxygen deposition (in Hungarian). T. Erdey-Gruz and I. Vajasdy (Inst. Phys. Chem. Radiology, Eötvös University, Budapest, Hungary). *Magyar Kém. Folyóirat*, 67 (1961) 90–95.
Die Polarisationsspannung (φ) der Sauerstoffentwicklung wurde von der Bearbeitung der Platinanode als unabhängig gefunden. Nach entsprechender, anodischer Vorpolarisation ist die Polarisationskurve (φ gegen log i aufgenommen, wo i die Stromdichte ist) im Interwall $3 \cdot 10^{-8} - 3 \cdot 10^{-4}$ A/cm² eine Gerade, deren Steigung von der Art der Bearbeitung und der Vorpolarisation unabhängig ist. Bei Anoden, die nur kurz vorpolarisiert wurden, verläuft die Gerade auch nach grösseren Stromdichten hin in gleicher Richtung. Nach längerer Vorpolarisation hingegen biegt die Kurve bei Stromdichten über $3 \cdot 10^{-4}$ A/cm² nach unten ab, d.h. der hier geschwindigkeitsbestimmende Vorgang erfordert in diesem Bereich eine geringere Aktivierungsenergie. Bei sehr geringen Stromdichten biegt die Kurve um: bei kurzer Vorpolarisation ist das Polarisationsspannung hier geringer, bei längerer Polarisation grösser, als auf Grund der mittleren Stromdichten zu erwarten wäre. Unter diesen Umständen ist die Aktivierungsenergie des geschwindigkeitsbestimmenden Vorganges hier grösser als jene des mittleren Abschnittes. [Ja. Inc.]

358 – The second rapid step in the nucleophilic substitution of alkyl halides. II. Competitive substitution reactions. D. Colomb (Weizmann Inst. of Science, Rehovah, Irsael). *J. Chem. Soc.*, (1959) 1334–1338.
The course of competitive substitution reactions of some alkyl halides is outlined, in which the ionic substituent (azide or thiocyanate) competes with a molecular species (water) for the same carbonium ion (triphenylmethyl, diphenylmethyl, *d-p*-tolylmethyl) yielding the alkyl azide or thiocyanate and the alcohol, all of which are stable. The combinations of the solvents and presence of various additives affect differently the activities of the reacting species and, in particular that of the carbonium ion and ionic substituent, as was shown by analysis. Decrease in dielectric constant usually increases the ratio of alkyl azide, or thiocyanate, to alcohol. An increase of ionic strength, however, decreases it. [G. F. Rey.]

359 – The anodic behaviour of a cathodically prepolarized bright platinum electrode in sulfuric acid solution. S. Shibata (Dept. of Chem., Faculty of Liberal Arts and Science, Yamagata University, Koshirakawa, Yamagata, Japan). *Bull. Chem. Soc., Japan*, 33 (1960) 1635–1640.
The anodic charging curves of a cathodically prepolarized bright platinum electrode in 1 *N* sulfuric acid solution saturated with hydrogen were studied with a mechanical oscillograph. The charging curves show four stages: a stage of steady potential (stage α′), then a slow rise of potential, followed by a rapid linear rise and finally a slow linear change.
Stage α′ is explained on the assumption that molecular hydrogen accumulates in the vicinity of

the electrode during the cathodic prepolarization, and that the concentration of this accumulated hydrogen decreases according to a first-order relationship. [H.H.Ba.]

360 – Behaviour of some impurities in the electro-refining of iron. S. Oka, T. Mukaibo and H. Aikawa (Dept. of Applied Chem., Faculty of Engineering, The University of Tokyo, Hongo, Tokyo, Japan). *Bull. Chem. Soc. Japan*, 33 (1960) 1680–1682.
The behaviour of trace impurities in the production of electrolytic iron was studied by the use of radio-tracers. Phosphate ions were found to deposit on the cathode, suggesting the formation of a positively charged complex. Deposited sulfur (from sulfate solution) could be removed by washing and wet polishing. Silver was effectively eliminated during electrolysis, but zinc was almost quantitatively deposited. [H.H.Ba.]

361 – Citrate buffer of defined ionic strength having no neutral electrolytes (in German). P. Kratochvíl and P. Munk (Inst. of Macromolecular Chem., Academy of Sciences, Prague, Czechoslovakia). *Collect. Czechoslov. Chem. Communs.*, 26 (1961) 593–595.
The buffer is prepared by mixing calculated amounts of citric acid and sodium hydroxide solutions of precisely known concentrations. The calculations are described in detail, the dependence of the dissociation constant values, which are calculated from the concentrations, on ionic strength being taken into account. The influence of ionic strength on the values of the dissociation constants are tabulated. Examples of calculated and measured pH values are given. [Ot.So.]

See also abstract no. 283.

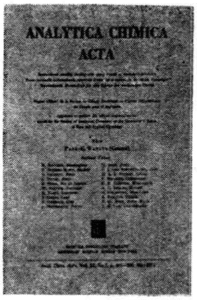
VOL. 3 NO. 1 JOURNAL OF ELECTROANALYTICAL CHEMISTRY JANUARY 1962

CONTENTS

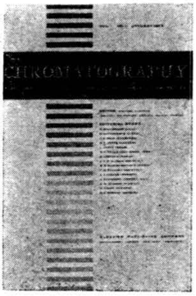
Revue générale

Original papers

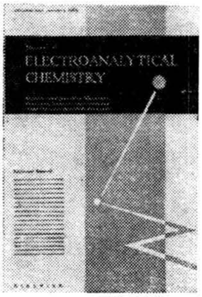
ELSEVIER PUBLISHING COMPANY, AMSTERDAM
Printed in The Netherlands by
NEDERLANDSE BOEKDRUK INRICHTING N.V., 'S-HERTOGENBOSCH



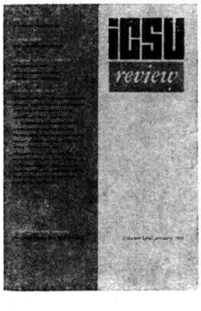
ANALYTICA CHIMICA ACTA



CHROMATOGRAPHY

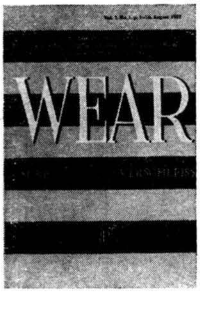


ELECTROANALYTICAL CHEMISTRY



ICSU review

LESS-COMMON METALS



WEAR