

Journal of

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*International Journal Dealing with all Aspects
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Including Fundamental Electrochemistry*

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Medical University Clinic, Zürich (Switzerland)

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6 × 9" x + 214 pages 31 tables 74 illus. 1957

Contents

1. Introduction. 2. Electrical Conduction of Solutions. 3. Theoretical Considerations. 4. Technique of Paper Electrophoresis. 5. Continuous Electrophoretic Separation. 6. Electrophoresis on the Cytoscale. 7. Combination of Chromatography and Electrophoresis. 8. Organic Acids. 9. Carbohydrates and Hydroxycompounds. 10. Nitrogen Compounds. 11. Alkaloids. 12. Proteins. 13. Nucleic Acids and Derivatives, and Phosphate Esters. 14. Antibiotics. 15. Triterpenoids. 16. Steroids. 17. Dyes. 18. Inorganic Compounds. 19. Physico-chemical Studies. 20. Electrophoresis in Packed Columns. 21. Electrophoresis Inside Gels. 22. Measurement of Diffusion Rates Inside Porous Media. 23. Electrokinetic Ultrafiltration. Author Index. Subject Index.

REVUE GÉNÉRALE

RAPPORT DE LA COMMISSION C.I.T.C.E.*
 "NOMENCLATURE ET DEFINITIONS ELECTROCHIMIQUES"
 ET DE LA SOUS-COMMISSION I.U.P.A.C.**
 "SYMBOLES ET TERMINOLOGIE ELECTROCHIMIQUES"

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(Reçu le 1 février, 1961)

Le présent rapport, auquel la Commission travaille depuis plusieurs années, a été mis au point en vue de sa présentation à la Section de Chimie Physique de l'Union Internationale de Chimie Pure et Appliquée au cours d'une réunion spéciale de la Commission C.I.T.C.E. de "Nomenclature et Définitions Electrochimiques" fonctionnant simultanément comme Sous-Commission de "Symboles et Terminologie Electrochimiques" de la Commission I.U.P.A.C. d'Electrochimie. Cette réunion a eu lieu à Bruxelles les 31 août, 1 et 2 septembre, 1960. Ce rapport doit être considéré comme une série de recommandations soumises par la Commission d'Electrochimie de l'I.U.P.A.C. à la Section de Chimie Physique et ainsi à l'I.U.P.A.C. entière.

Le personnel de la Commission C.I.T.C.E. et de la Sous-Commission I.U.P.A.C. a varié au cours des années, mais les membres actifs suivants ont participé à la préparation de toutes les versions précédentes de ce rapport et, en particulier, à la rédaction du texte ci-dessous: RAYMOND DEFAY (Université de Bruxelles), ERICH LANGE (Université d'Erlangen), GIULIO MILAZZO (Istituto Superiore di Sanità, Rome), GABRIEL VALENSI (Université de Poitiers) et PIERRE VAN RYSSELBERGHE (Université Stanford).

SYMBOLES DES GRANDEURS ELECTROCHIMIQUES ET CONNEXES

Grandeurs extensives

\tilde{E} ou \tilde{U}	(voir II(4))	Energie électrochimique, ou simplement énergie.
E ou U	(II(4)(e))	Energie chimique.
\tilde{H}	(II(4)(a))	Enthalpie électrochimique
H	(II(4)(d))	Enthalpie chimique.
\tilde{S}	(II(5)(a))	Entropie électrochimique, ou simplement entropie.
\tilde{F}	(II(5)(a))	Energie libre électrochimique.
F	(II(6)(e))	Energie libre chimique.
\tilde{G}	(II(6)(a))	Enthalpie libre électrochimique.
G	(II(6)(d))	Enthalpie libre chimique.

* C.I.T.C.E. = Comité International de Thermodynamique et de Cinétique Electrochimiques.

** I.U.P.A.C. = Union Internationale de Chimie Pure et Appliquée.

V		Volume total du système.
V^α ou V_α		Volume de la phase α .
n		Valeur numérique de la quantité totale de matière contenue dans le système, exprimée en moles (ou en multiples ou sous-multiples de la mole).
N		Valeur numérique de la quantité totale de matière contenue dans le système, exprimée en molécules ou atomes. On a: quantité de matière = n moles = N molécules (ou atomes).
n^α ou n_α		Voir n plus haut. Phase α au lieu du système total.
N^α ou N_α		Voir N plus haut. Phase α au lieu du système total.
n_i^α ou $n_{i,\alpha}$		Voir n plus haut. Substance i dans phase α .
N_i^α ou $N_{i,\alpha}$		Voir N plus haut. Substance i dans phase α .
n_i		Voir n plus haut. Quantité totale de substance i dans le système.
N_i		Voir N plus haut. Quantité totale de substance i dans le système.
$N_0 = 6.023 \cdot 10^{23}$		Nombre d'Avogadro (dans la littérature de langue allemande souvent appelé nombre de Loschmidt).
q		Charge électrique.
<i>Grandeurs intensives</i>		
T		Température absolue dans l'échelle Kelvin.
p		Pression extérieure.
m_i	(IV(15)(a))	Molalité du constituant dissous i d'une solution.
x_i ou N_i	(IV(15)(a))	Titre molaire du constituant dissous i d'une solution.
C_i	(IV(15)(a))	Molarité du constituant dissous i d'une solution.
\tilde{h}_i^α ou $\tilde{h}_{i,\alpha}$	(II(4)(b))	Enthalpie électrochimique partielle molaire du constituant i dans la phase α , égale à
		$(\partial \tilde{H} / \partial n_i^\alpha)_{T, p, n_j^\alpha}$, avec $j \neq i$
$\tilde{\mu}_i^\alpha$ ou $\tilde{\mu}_{i,\alpha}$	(II(5)(b), II(6)(b))	Potentiel électrochimique du constituant i dans la phase α , égal à
		$(\partial \tilde{G} / \partial n_i^\alpha)_{T, p, n_j^\alpha}$, avec $j \neq i$
ψ^α ou ψ_α	(II(3))	Potentiel électrique intérieur de la phase α .
φ^α ou φ_α	(II(1))	Potentiel électrique extérieur de la phase α .
χ^α ou χ_α	(II(2))	Tension électrique de surface de la phase α . On a:
		$\varphi^\alpha = \psi^\alpha + \chi^\alpha$
z_i		Nombre algébrique de charges élémentaires positives portées par un ion d'espèce i .
F		Charge molaire d'un cation monovalent. Si l'unité de quantité de substance est la mole, cette charge s'identifie à celle du faraday ($F = 95487$ coulombs).

h_i^α ou $h_{i,\alpha}$ (II(4)(c) Enthalpie chimique partielle molaire du constituant i dans la phase α . On a :

$$\tilde{h}_i^\alpha = h_i^\alpha + z_i F \varphi^\alpha.$$

μ_i^α ou $\mu_{i,\alpha}$ (II(5)(c), II(6)(c) Potentiel chimique du constituant i dans la phase α . On a :

$$\tilde{\mu}_i^\alpha = \mu_i^\alpha + z_i F \varphi^\alpha.$$

w_i^α ou $w_{i,\alpha}$ (II(7) Travail d'extraction du constituant i de la phase α .
 ω_i^α ou $\omega_{i,\alpha}$ (II(8) Tension d'extraction du constituant i de la phase α .

Grandeurs attachées aux réactions électrochimiques

ξ (III(8) Avancement de la réaction.
 ν_i^α ou $\nu_{i,\alpha}$ Coefficient stoechiométrique du constituant i dans la phase α avec son signe (pris positif pour tout constituant du membre de droite de la réaction et pris négatif pour tout constituant du membre de gauche).

z (III(9), IV(6) Nombre de charges transportées par la réaction.

τ_i^α ou $\tau_{i,\alpha}$ (III(24) Nombre d'enrichissement du constituant i dans la phase α .

$\Delta\tilde{G}$ (III(10), IV(7) Enthalpie libre électrochimique de la réaction.

\tilde{A} (III(11), IV(7) Affinité électrochimique de la réaction. On a :

$$\tilde{A} = - \sum_\gamma \sum_\alpha \nu_\gamma^\alpha \tilde{\mu}_\gamma^\alpha = -\Delta\tilde{G}.$$

$\Delta G = (\partial G / \partial \xi)_{T,p}$ (III(12), IV(8) Enthalpie libre chimique de la réaction.

A (III(13), IV(8) Affinité chimique de la réaction. On a :

$$A = - \sum_\gamma \sum_\alpha \nu_\gamma^\alpha \mu_\gamma^\alpha = -\Delta G.$$

$\Delta H = (\partial H / \partial \xi)_{T,p}$ (III(14) Enthalpie chimique de la réaction. On a :
 $= h_{T,p}$

$$\Delta H = \sum_\gamma \sum_\alpha \nu_\gamma^\alpha h_\gamma^\alpha.$$

$r_{T,p} = -\Delta H$ (III(15) Chaleur chimique de réaction, à T et p constants.
 $r_{T,V} = -(\partial E / \partial \xi)_{T,V}$ Chaleur chimique de réaction, à T et V constants.

Systèmes à deux phases (par exemple une électrode I|II)

$\varepsilon^{I/II} = A / zF$ (III(21) Tension chimique entre la phase I et la phase II.

$g^{I/II} = \varphi^I - \varphi^{II}$ (III(6), III(19) Tension Galvani entre la phase I et la phase II.

$v^{I/II} = \psi^I - \psi^{II}$ (III(5) Tension Volta entre la phase I et la phase II. On a :

$$v^{I/II} = g^{I/II} - (\chi^I - \chi^{II}).$$

$g_{rév.}^{I/II} = -\varepsilon^{I/II}$ (III(22)) Tension Galvani d'équilibre entre la phase I et la phase II. On a:

$$g_{rév.}^{I/II} = -A/zF.$$

$\tilde{\varepsilon}^{I/II} = \varepsilon^{I/II} + g^{I/II}$ (III(20)) Tension électrochimique entre la phase I et la phase II. On a:

$$\tilde{\varepsilon}^{I/II} = g^{I/II} - g_{rév.}^{I/II}.$$

Cellules galvaniques

$\mathcal{E} = A/zF$ (IV(10)) Tension chimique (ou force électromotrice) de la cellule.

$\mathcal{U} = \varphi^1 - \varphi^{1'}$ (IV(4)) Tension électrique de la cellule.

$\mathcal{U}_{rév.} = -\mathcal{E} = -A/zF$ (IV(8)) Tension électrique réversible ou d'équilibre de la cellule.

$\tilde{\mathcal{E}} = \mathcal{U} + \mathcal{E} = \mathcal{U} - \mathcal{U}_{rév.}$ (IV(9), IV(11)) Tension électrochimique de la cellule.

Pour certaines grandeurs définies dans le présent rapport nous ne faisons aucune recommandation explicite quant à leurs symboles. Ceci signifie que, dans ces cas, nous nous rallions aux recommandations de la Commission I.U.P.A.C. de Symboles et de Terminologie Physico-Chimiques. Quelques différences de points de vue et de préoccupations entre les travaux de cette Commission et ceux de la nôtre nous ont amenés à présenter certaines recommandations parallèles. De plus, dans le cas particulier des diverses tensions, nous considérons des concepts et symboles que cette autre Commission n'a pas examinés.

I. DÉFINITIONS GÉNÉRALES

(1) On appelle *cation* un atome ou un groupement d'atomes porteur d'une charge nette positive.

(2) On appelle *anion* un atome ou un groupement d'atomes porteur d'une charge nette négative.

(3) Rappelons que la *force d'image* est la force électrostatique qui s'exerce entre une charge extérieure à un conducteur et ce conducteur par suite de la charge électrostatique induite dans le conducteur par la charge extérieure considérée. A la distance de 10^{-4} cm la contribution des forces d'image au travail molaire d'extraction (voir II(7)) de l'électron ou d'un ion monovalent n'est que de l'ordre de 10 calories.

Le *potentiel électrique* dans le vide et à distance suffisante de tout système matériel (c'est à dire au-delà du rayon d'action pratique des forces d'image) est défini de la manière suivante: Une charge ponctuelle q , dépourvue de tout support matériel, est amenée infiniment lentement de l'infini au point considéré avec une dépense de travail w . Le *potentiel électrique* est la limite du quotient w/q lorsque q tend vers zéro. Pendant cette opération, les champs électrique et magnétique agissant sur la charge ponctuelle sont considérés comme étant stationnaires.

(4) La *tension électrique* d'un point 1 à un point 2 est égale au potentiel électrique au point 1 diminué du potentiel électrique au point 2.

(5) La *différence de potentiel électrique* correspondant à un intervalle 1-2 est égale au potentiel électrique au point 2 diminué du potentiel électrique au point 1.

La différence de potentiel électrique est donc égale en valeur absolue, mais de signe opposé à la tension électrique.

Le champ électrique E en un point est relié au potentiel électrique φ en ce point par la relation $E = -\text{grad } \varphi$. Dans le cas d'une coordonnée spatiale unique x , on écrit $E = -d\varphi/dx$, ou, lorsque le champ est uniforme dans l'intervalle Δx , $E = -\Delta\varphi/\Delta x = \mathcal{U}/\Delta x$, \mathcal{U} désignant la tension électrique entre l'origine et l'extrémité de l'intervalle Δx . La différence de potentiel électrique définie en I(5) est donc égale à l'accroissement $\Delta\varphi$ figurant dans la dernière formule ci-dessus.

II. SYSTÈMES ÉLECTROCHIMIQUES À UNE PHASE

(1) Le potentiel électrique extérieur ψ d'une phase conductrice, dont la surface limitrophe est uniforme, est celui défini dans la théorie classique de l'électricité et pris, dans le vide, immédiatement au-delà du rayon d'action pratique des forces d'image, c'est à dire à une distance de l'ordre de 10^{-4} cm de la surface géométrique extérieure de la phase.

Cette quantité est mesurable.

(2) Pour transférer la charge q considérée en I(3) du point où a été défini le potentiel électrique extérieur ψ jusqu'à un point au sein de la phase, l'existence d'une couche de charges et de dipôles orientés nécessite une quantité de travail électrique w' à fournir contre les forces coulombiennes macroscopiques. La limite du rapport w'/q , lorsque q tend vers zéro, est égale à la *tension électrique de surface* χ .

Cette tension est positive quand, au travers de la couche superficielle, le potentiel électrique augmente de l'extérieur à l'intérieur de la phase.

(3) Le *potentiel électrique intérieur* φ en un point d'une phase est égal à la somme du potentiel électrique extérieur et de la tension électrique de surface:

$$\varphi = \psi + \chi$$

Autrement dit, c'est le potentiel que calculerait l'électrostatique à partir de la répartition macroscopique des densités de charge par unité de volume ou de surface et des polarisations moléculaires par unité de volume.

Le potentiel électrique intérieur est une grandeur définissable en principe, mais généralement non-mesurable.

(4) Nous considérons un système comprenant toutes les phases et portions de matière, en contact l'une avec l'autre ou séparées par du vide ou par un milieu ambiant quelconque, dont les charges électriques macroscopiques éventuelles (réparties dans les volumes ou sur les surfaces extérieures des phases) et les polarisations moléculaires affectent de manière non-négligeable le potentiel électrique en un point quelconque de ce système. Un tel système sera désigné *système électrochimique englobant toutes les charges agissantes*.

(a) Dans un tel système, l'enthalpie électrochimique \tilde{H} est définie comme étant l'énergie \tilde{E} du système augmentée du produit de la pression extérieure p par le volume total V du système:

$$\tilde{H} = \tilde{E} + pV$$

(b) L'*enthalpie électrochimique partielle molaire* \tilde{h}_i^α d'un constituant i d'une phase α est la dérivée partielle, par rapport au nombre de moles de ce constituant dans cette

phase, de l'enthalpie électrochimique du système englobant toutes les charges agissantes. Dans cette différentiation, on maintient constants tous les autres nombres de moles, la température et la pression extérieure:

$$\tilde{h}_i^\alpha = \left(\frac{\partial \tilde{H}}{\partial n_i^\alpha} \right)_{T, p, n_j^\beta, \dots}$$

(c) L'enthalpie chimique partielle molaire h_i^α d'un constituant i d'une phase α est égale à l'enthalpie électrochimique partielle molaire de ce constituant dans cette phase diminuée du produit de la charge molaire de ce constituant, $z_i F$ ($F = 1$ faraday), par le potentiel électrique intérieur de cette phase, φ^α :

$$h_i^\alpha = \tilde{h}_i^\alpha - z_i F \varphi^\alpha$$

(d) L'enthalpie chimique H du système est la somme, étendue à tous les constituants et à toutes les phases, des produits des enthalpies chimiques partielles molaires par les nombres de moles correspondants:

$$H = \sum_{\alpha} \sum_i n_i^\alpha h_i^\alpha$$

(e) L'énergie chimique E du système est égale à son enthalpie chimique diminuée du produit de la pression extérieure par le volume total du système:

$$E = H - pV$$

(5) (a) Dans un système électrochimique englobant toutes les charges agissantes, l'énergie libre électrochimique (de HELMHOLTZ) \tilde{F} est définie comme étant l'énergie du système diminuée du produit de la température par l'entropie du système:

$$\tilde{F} = \tilde{E} - T\tilde{S}$$

(b) Le potentiel électrochimique $\tilde{\mu}_i^\alpha$ d'un constituant d'une phase est la dérivée partielle, par rapport au nombre de moles de ce constituant dans cette phase, de l'énergie libre électrochimique du système englobant toutes les charges agissantes. Dans cette différentiation, on maintient constants tous les autres nombres de moles, la température, les volumes des phases et la configuration géométrique du système:

$$\tilde{\mu}_i^\alpha = \left(\frac{\partial \tilde{F}}{\partial n_i^\alpha} \right)_{T, V, n_j^\beta, \dots}$$

(c) Le potentiel chimique μ_i^α d'un constituant d'une phase est égal au potentiel électrochimique de ce constituant dans cette phase diminué du produit de la charge molaire de ce constituant par le potentiel électrique intérieur de cette phase:

$$\mu_i^\alpha = \tilde{\mu}_i^\alpha - z_i F \varphi^\alpha$$

(6) (a) Dans un système électrochimique englobant toutes les charges agissantes, l'enthalpie libre électrochimique \tilde{G} est définie comme étant l'énergie libre électrochimique du système augmentée du produit de la pression extérieure par le volume total du système:

$$\tilde{G} = \tilde{F} + pV$$

(b) L'enthalpie libre électrochimique partielle molaire d'un constituant d'une phase est la dérivée partielle, par rapport au nombre de moles de ce constituant dans cette phase, de l'enthalpie libre électrochimique du système englobant toutes les charges agissantes. Dans cette différentiation, on maintient constants tous les autres nombres de moles, la température et la pression extérieure.

L'enthalpie libre électrochimique partielle molaire est identique au *potentiel électrochimique* défini en II(5) (b):

$$\tilde{\mu}_i^\alpha = \left(\frac{\partial \tilde{G}}{\partial n_i^\alpha} \right)_{T, p, n_j^\beta, \dots}$$

(c) L'enthalpie libre chimique partielle molaire d'un constituant d'une phase est égale à l'enthalpie libre électrochimique partielle molaire de ce constituant dans cette phase diminuée du produit de la charge molaire de ce constituant par le potentiel électrique intérieur de cette phase.

L'enthalpie libre chimique partielle molaire est identique au *potentiel chimique* défini en II(5) (c):

$$\mu_i^\alpha = \tilde{\mu}_i^\alpha - z_i F \varphi^\alpha$$

(d) L'enthalpie libre chimique G du système est la somme, étendue à tous les constituants et à toutes les phases, des produits des potentiels chimiques par les nombres de moles correspondants:

$$G = \sum_i \sum_\alpha n_i^\alpha \mu_i^\alpha$$

(e) L'énergie libre chimique (de HELMHOLTZ) F du système est égale à son enthalpie libre chimique diminuée du produit de la pression extérieure par le volume total du système:

$$F = G - pV$$

(7) Considérons un constituant d'une phase conductrice. Le *travail molaire d'extraction* de ce constituant de cette phase est le travail qu'il faut dépenser pour déplacer une mole de ce constituant de l'intérieur de la phase, où règne le potentiel électrique intérieur φ^α , à la distance extérieure à la phase où règne le potentiel électrique extérieur ψ^α (voir II(1) et II(3)).

Le travail molaire d'extraction comprend un terme coulombien $w_{ie} = z_i F(\psi^\alpha - \varphi^\alpha) = -z_i F \chi^\alpha$ et un terme chimique $w_{ic} = \mu_{is} - \mu_i^\alpha$, μ_{is} étant le potentiel chimique du constituant i dans l'état fictif de SCHOTTKY. Rappelons que l'état fictif de SCHOTTKY est un état idéal dans lequel les ions du constituant se trouvent immobilisés (c'est à dire dépourvus d'énergie cinétique de translation) à des distances suffisantes l'un de l'autre pour que les forces interioniques puissent être négligées, seuls les degrés de liberté internes des ions apportant chacun l'énergie qui correspond à l'équilibre statistique pour la température envisagée. Le potentiel électrochimique étant donné par $\tilde{\mu}_i^\alpha = \mu_i^\alpha + z_i F \varphi^\alpha$, avec $\varphi^\alpha = \psi^\alpha + \chi^\alpha$, on a, en prenant l'état de SCHOTTKY comme zéro de potentiel chimique:

$$w_i = w_{ie} + w_{ic} = z_i F \psi^\alpha - \tilde{\mu}_i^\alpha = -z_i F \chi^\alpha - \mu_i^\alpha$$

Le travail molaire d'extraction w_i et la tension correspondante (voir II(8)) sont des quantités mesurables.

(8) La valeur absolue du quotient du travail molaire d'extraction d'un constituant

d'une phase par la charge molaire de ce constituant est la *tension d'extraction* de ce constituant de cette phase.

La tension d'extraction peut être considérée comme la somme de deux tensions: une première correspondant à l'extraction "chimique" de la phase et une seconde correspondant à l'extraction à travers la barrière due à la tension électrique de surface.

Notons qu'il est souvent fait usage d'un travail d'extraction exprimé en volts obtenu en divisant le travail molaire d'extraction défini plus haut par la charge molaire exprimée en coulombs. L'usage de notre nouvelle définition du travail molaire d'extraction et celui de la notion de tension d'extraction sont plus corrects du point de vue dimensionnel.

La définition ci-dessus de la tension d'extraction s'applique sans ambiguïté à des ions de charge quelconque.

Le travail molaire d'extraction peut s'exprimer en kilocalories, en joules ou en faradays volts. La tension d'extraction s'exprime en volts.

(g) (a) La *migration électrochimique* ou *diffusion électrochimique* d'un constituant chargé d'une phase est le déplacement de ce constituant d'une région de la phase à une autre région de cette même phase résultant d'une différence entre les valeurs du potentiel électrochimique de ce constituant en ces deux régions.

Cette définition s'applique également à un constituant dipolaire dans un champ non-uniforme.

L'expression *migration électrochimique* s'emploiera de préférence lorsque la différence entre les valeurs du potentiel électrochimique est due principalement à la différence de potentiel électrique entre les deux régions, tandis que l'expression *diffusion électrochimique* s'emploiera de préférence lorsque la différence entre les valeurs du potentiel électrochimique est due principalement à la différence de potentiel chimique entre les deux régions (cas typique de la polarographie, par exemple).

La *force électrochimique molaire* appliquée à un constituant chargé d'une phase est égale à moins le gradient du potentiel électrochimique de ce constituant. La *force électrochimique par particule* est égale à cette quantité divisée par le nombre d'Avogadro.

(b) La *migration électrique*, ou plus brièvement la *migration* d'un constituant chargé non-dipolaire d'une phase est le déplacement de ce constituant d'une région de la phase à une autre région de cette même phase résultant d'une différence entre les valeurs du potentiel électrique en ces deux régions, le potentiel chimique de ce constituant ayant la même valeur en ces deux régions.

La *force électrique molaire* appliquée à un constituant chargé non-dipolaire d'une phase est égale à moins le gradient du potentiel électrique (c'est à dire à plus le champ électrique) multiplié par la charge molaire de ce constituant. La *force électrique par particule* est égale à cette quantité divisée par le nombre d'Avogadro.

(c) La *diffusion chimique*, ou plus brièvement la *diffusion* d'un constituant neutre d'une phase (par exemple la diffusion simultanée de deux espèces ioniques produites par la dissociation d'un électrolyte neutre) est le déplacement de ce constituant d'une région de la phase à une autre région de cette même phase résultant d'une différence entre les valeurs du potentiel chimique de cette espèce neutre en ces deux régions.

On peut semblablement définir la diffusion d'une espèce ionique dans le cas où la différence de potentiel électrique entre les deux régions est nulle ou négligeable. Lorsque ceci n'est pas le cas, on est ramené à la définition II(g) (a).

La *force chimique molaire* appliquée à un constituant d'une phase est égale à moins

le gradient du potentiel chimique de ce constituant. La *force chimique par particule* est égale à cette quantité divisée par le nombre d'Avogadro.

Le *coefficient de diffusion* D_i d'une espèce neutre ou ionique i est défini par la loi de Fick :

$$J_i = -D_i \text{ grad } C_i$$

qui relie au gradient de la concentration C_i de l'espèce i son flux de diffusion J_i par unité de surface dans la direction de ce gradient. On a :

$$J_i = dn_i/dt = C_i v_i$$

où dn_i représente le nombre de moles de l'espèce i traversant pendant le temps dt une surface d'aire unité perpendiculaire au gradient de C_i et où v_i représente la vitesse de diffusion des particules de l'espèce i . Les deux relations ci-dessus s'écrivent localement en chaque point de la phase.

Un examen plus détaillé du concept de coefficient de diffusion ne peut trouver place dans le cadre du présent rapport.

(10) La résistance de frottement exercée sur une particule par un milieu donné étant supposée proportionnelle à la vitesse de cette particule, on désignera par *mobilité* de cette particule la vitesse stationnaire qu'elle acquiert sous l'action d'une force unité.

Quand la particule envisagée est chargée, on désignera plus spécialement par *mobilité électrique* de cette particule la vitesse stationnaire qu'elle acquiert sous l'action d'un champ électrique unité.

La *mobilité électrique limite* d'un ion est la valeur de sa mobilité électrique dans le solvant exempt d'électrolytes (voir II(12)).

(11) La *conductibilité électrique* d'un système est la propriété de ce système de laisser circuler des charges électriques sous l'influence d'un champ électrique.

(12) Toute phase douée de conductibilité électrique est appelée *conducteur*.

Un conducteur est dit de *première classe* ou *électronique* lorsque les charges électriques mobiles de ce conducteur sont uniquement des électrons. C'est le cas des métaux purs.

Un conducteur est dit de *seconde classe* ou *ionique* lorsque les charges électriques mobiles de ce conducteur sont des anions et des cations.

Un *électrolyte* est un corps pur manifestant la conductibilité de seconde classe à l'état solide, liquide ou dissous.

Un conducteur est dit *mixte* lorsque les charges électriques mobiles de ce conducteur sont les unes des électrons, les autres des ions. Certains oxydes et sels métalliques sont des conducteurs mixtes à l'état cristallin.

(13) La *conductance* d'un système est l'inverse de sa résistance électrique. C'est donc la valeur arithmétique de la charge qu'il transmet, par unité de temps et en régime stationnaire, lorsqu'une tension électrique égale à l'unité est appliquée entre ses extrémités.

(14) La *conductivité* d'une phase, égale à l'inverse de sa *résistivité*, est la conductance d'un conducteur découpé dans cette phase ayant une longueur unité dans la direction du champ électrique et une section d'aire unité dans un plan perpendiculaire à ce champ.

(15) La *conductibilité équivalente* d'un électrolyte solide, liquide ou dissous est le quotient de sa conductivité par sa concentration exprimée en équivalents-grammes par unité de volume.

Dans le cas d'un électrolyte entièrement dissocié en ses ions, cette conductibilité équivalente est égale au produit du faraday par la somme des mobilités électriques de l'anion et du cation.

La *conductibilité équivalente limite* d'un électrolyte est sa conductibilité équivalente à dilution infinie.

La *conductibilité ionique équivalente* d'un ion est égale au produit du faraday par la mobilité électrique de cet ion.

La *conductibilité ionique équivalente limite* d'un ion est égale au produit du faraday par la mobilité électrique limite de cet ion.

(16) La *conductibilité molaire* d'un électrolyte solide, liquide ou dissous est le quotient de sa conductivité par sa concentration exprimée en moles par unité de volume. Elle est donc égale à la conductibilité équivalente multipliée par le nombre d'équivalents-grammes qui constituent une mole de l'électrolyte.

La *conductibilité molaire limite* d'un électrolyte est sa conductibilité molaire à dilution infinie.

(17) Le *nombre de transport* d'une espèce ionique, présente ou considérée comme présente dans un système, est le quotient de la quantité d'électricité que transporte cette espèce ionique au cours de sa migration (voir II(9) (b)) par la quantité totale d'électricité transportée par toutes les espèces chargées, présentes ou considérées comme présentes dans le système.

Un examen plus détaillé du concept de nombre de transport ne peut trouver place dans le cadre du présent rapport.

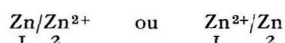
(18) L'usage courant en chimie physique et en électrochimie a été d'exprimer les valeurs numériques des diverses grandeurs, et notamment de celles définies plus haut, dans un système d'unités mixtes comprenant, d'une part, les unités CGS (ou leurs multiples et sous-multiples) pour les longueurs, masses, temps et grandeurs dérivées de ces dimensions fondamentales et, d'autre part, les unités électriques pratiques (coulomb, ampère, volt, etc., ou leurs multiples et sous-multiples). Pour l'énergie ou le travail, diverses autres unités ont été employées en plus de l'unité CGS erg: le joule, le kilogramme-mètre, la calorie, la kilocalorie, sans parler des unités du Système Impérial Britannique.

Répondant à une enquête ouverte par la Section de Chimie Physique de l'Union Internationale de Chimie Pure et Appliquée, notre Commission a recommandé que le système M.K.S.A., déjà adopté officiellement par de nombreuses organisations internationales, soit dorénavant employé le plus possible en chimie physique et, surtout, de manière aussi rapide et générale que possible, en électrochimie.

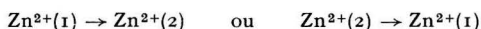
III. SYSTÈMES ÉLECTROCHIMIQUES À DEUX PHASES

(1) Un *système électrochimique à deux phases* ou, dans le sens le plus général du mot, une *électrode* est un système constitué de deux phases en contact pouvant être le siège d'une *réaction d'électrode*, c'est à dire une réaction à laquelle participent certains constituants des deux phases et par laquelle un transfert de charge a lieu du sein d'une des phases au sein de l'autre phase.

Les phases de l'électrode sont représentées par un schéma et numérotées 1, 2 de gauche à droite. Par exemple:



La réaction d'électrode peut être écrite de chacune des deux manières suivantes pour chacun des deux schémas:



A chacune des quatre combinaisons schéma-réaction correspondent une charge réactionnelle et un nombre de charges transportées (voir III(9)).

(2) Dans un sens plus restreint, on appelle *électrode* un système métal/électrolyte ou métal/solution d'un ou plusieurs électrolytes.

Dans un sens encore plus restreint, on appelle souvent *électrode* la phase métallique d'un système métal/électrolyte ou métal/solution. Dans tout ce rapport les mots *métal* et *métallique* pourront se rapporter à un conducteur de première classe quelconque.

(3) Par rapport à la direction conventionnelle du courant (qui est opposée à celle du mouvement des électrons dans les parties métalliques), chaque phase d'une cellule (voir Partie IV) possède une *face d'entrée* et une *face de sortie*.

(4) Un conducteur métallique en contact avec une solution fonctionne comme *cathode* vis-à-vis de la solution si sa face en contact avec la solution est face d'entrée dans le métal. Vice-versa, un conducteur métallique en contact avec une solution fonctionne comme *anode* vis-à-vis de la solution si sa face en contact avec la solution est face de sortie du métal.

(5) La *tension Volta* d'une phase 1 par rapport à une phase 2 est égale au potentiel électrique extérieur de la phase 1 diminué du potentiel électrique extérieur de la phase 2, lorsque ces deux phases sont en contact.

(6) La *tension Galvani* d'une phase 1 par rapport à une phase 2 est égale au potentiel électrique intérieur de la phase 1 diminué du potentiel électrique intérieur de la phase 2, lorsque ces deux phases sont en contact.

(7) Dans toute région interphase on admet l'existence d'une *double couche électrochimique*, appellation dont nous recommandons l'usage à la place de "double couche électrique" et surtout de "double couche électrolytique".

La double couche électrochimique d'une électrode en l'absence de courant commence, du côté métallique, à la surface parallèle à l'électrode à partir de laquelle les potentiels chimiques des constituants du métal (ions métalliques et électrons) commencent à différer de leurs valeurs au sein du métal; elle s'étend, du côté de la solution, jusqu'à la surface parallèle à l'électrode au-delà de laquelle les potentiels chimiques de toutes les espèces dissoutes deviennent égaux à leurs valeurs au sein de la solution.

Du côté de la solution, la double couche peut être décomposée en deux portions. Celle qui est contiguë au métal possède certaines propriétés caractéristiques des couches d'adsorption et les potentiels chimiques standard de ses constituants sont en général différents des potentiels chimiques standard correspondants au sein de la solution. L'autre portion, qui est contiguë à la solution, est appelée *couche diffuse* et les potentiels chimiques standard de ses constituants sont égaux aux potentiels chimiques standard au sein de la solution.

(8) Nous préconisons l'adoption de la notion quantitative d'*avancement d'une réaction*:

Lorsque, à partir d'un état initial donné, une réaction a avancé de telle manière que, de chaque constituant figurant dans le second membre de l'équation stoechiométrique, il se soit formé un nombre de moles égal au coefficient stoechiométrique de ce constituant, on dira que la réaction a avancé d'une *unité d'avancement*.

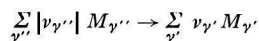
(9) La *charge réactionnelle* d'une réaction d'électrode est la charge transportée de la phase 1 à la phase 2 par la réaction d'électrode lorsque celle-ci a avancé d'une unité d'avancement, c'est à dire lorsqu'elle a joué une fois de gauche à droite. La charge réactionnelle peut être positive ou négative.

Le *nombre de charges transportées* par une réaction d'électrode est le nombre de faradays transportés de la phase 1 à la phase 2 par la réaction d'électrode lorsque celle-ci a avancé d'une unité d'avancement. Ce nombre peut être positif ou négatif.

Si la charge réactionnelle est représentée par zF , le nombre de charges transportées est z .

(10) L'enthalpie libre électrochimique d'une réaction d'électrode est égale à la somme des potentiels électrochimiques des produits de la réaction multipliés respectivement par leurs coefficients stoechiométriques, diminuée de la somme des potentiels électrochimiques des réactifs de la réaction, multipliés respectivement par leurs coefficients stoechiométriques pris en valeurs absolues.

Ecrivons la réaction d'électrode de la manière suivante:



Nous avons alors:

$$\Delta\tilde{G} = \sum_{\gamma'} v_{\gamma'} \tilde{\mu}_{\gamma'} - \sum_{\gamma''} |v_{\gamma''}| \tilde{\mu}_{\gamma''} = \sum_{\gamma} v_{\gamma} \tilde{\mu}_{\gamma}$$

(11) L'affinité électrochimique d'une réaction d'électrode \tilde{A} est la quantité définie en III(10) prise avec le signe moins. Nous avons:

$$\tilde{A} = -\Delta\tilde{G} = -\sum_{\gamma} v_{\gamma} \tilde{\mu}_{\gamma}$$

A l'équilibre électrochimique \tilde{A} et $\Delta\tilde{G}$ sont nuls.

Le signe de l'affinité électrochimique détermine le sens d'avancement de la réaction. Si, pour un état chimique et physique donné du système, l'affinité électrochimique est positive, la réaction, telle qu'elle a été écrite, avance dans le sens positif ($d\xi/dt > 0$), c'est à dire progresse de gauche à droite. Lorsque l'affinité électrochimique est négative, la réaction avance de droite à gauche ($d\xi/dt < 0$).

(12) L'enthalpie libre chimique d'une réaction d'électrode ΔG s'exprime en fonction des potentiels chimiques des produits et réactifs de la réaction d'électrode de la même manière que l'enthalpie libre électrochimique de cette réaction s'exprime en fonction des potentiels électrochimiques des produits et réactifs (voir III(10)):

$$\Delta G = \sum_{\gamma'} v_{\gamma'} \mu_{\gamma'} - \sum_{\gamma''} |v_{\gamma''}| \mu_{\gamma''} = \sum_{\gamma} v_{\gamma} \mu_{\gamma}$$

(13) L'affinité chimique d'une réaction d'électrode A est la quantité définie en III(12) prise avec le signe moins:

$$A = -\Delta G = -\sum_{\gamma} v_{\gamma} \mu_{\gamma}$$

L'affinité électrochimique d'une réaction d'électrode est égale à la somme de son affinité chimique et d'une quantité pouvant être appelée *affinité électrique* égale au produit de la charge réactionnelle par la tension électrique de l'électrode.

(14) L'enthalpie chimique d'une réaction d'électrode ΔH est égale à la somme des enthalpies chimiques partielles molaires (voir II(4) (c)) des produits de la réaction, multipliées respectivement par leurs coefficients stoechiométriques, diminuée de la somme de enthalpies chimiques partielles molaires des réactifs de la réaction, multipliées respectivement par leurs coefficients stoechiométriques pris en valeurs absolues:

$$\Delta H = \sum_{\gamma'} v_{\gamma'} h_{\gamma'} - \sum_{\gamma''} |v_{\gamma''}| h_{\gamma''} = \sum_{\gamma} v_{\gamma} h_{\gamma}$$

(15) La *chaleur chimique à température et pression constantes d'une réaction d'électrode* r_{Tp} est la quantité définie en III(14) prise avec le signe moins :

$$r_{Tp} = -\Delta H = -\sum_{\gamma} \nu_{\gamma} h_{\gamma}$$

Cette chaleur ne doit pas être confondue avec la chaleur réellement dégagée par la réaction d'électrode. Celle-ci s'étudie dans le cadre de la théorie des chaleurs de Peltier. Dans le présent rapport il ne sera question que de la chaleur de Peltier à un contact intermétallique (voir III(16) et Partie V).

(16) (a) La *chaleur de Peltier* à un contact intermétallique 1/2 est la chaleur dégagée à ce contact lorsqu'un courant électrique positif traverse l'interface dans la direction 1-2.

(b) Le *coefficient de Peltier* π (1/2) est la chaleur de Peltier dégagée lors du passage de 1 coulomb à travers l'interface dans le sens 1-2 de la numérotation des phases.

(17) (a) Une *électrode simple* est une électrode à laquelle a lieu une réaction d'électrode unique.

(b) Une *polyélectrode* ou *électrode multiple* est une électrode à laquelle ont lieu plusieurs réactions d'électrode simultanées.

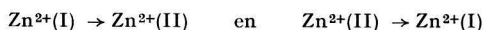
(18) Dans toutes les définitions précédentes l'ordre de succession des phases pouvait être choisi arbitrairement, ainsi que le sens d'écriture de la réaction. Les signes des grandeurs définies ci-dessus sont liés à ces choix.

Dans les définitions ci-après des tensions d'électrode l'*ordre de succession des phases est fixé conventionnellement* suivant le schéma : métal (I)/solution (II), le sens d'écriture de la réaction restant arbitraire.

(19) La *tension électrique d'une électrode* est égale au potentiel électrique intérieur du métal (I) diminué de celui de la solution (II). C'est donc une tension Galvani (voir III(6)).

(20) Si, pour un état chimique et électrique donné d'une électrode, on permute les membres de gauche et de droite de la réaction d'électrode, sans changer l'ordre de numérotation des phases, le quotient de l'affinité électrochimique de cette réaction d'électrode par la charge réactionnelle correspondante (telle qu'elle a été définie en III(9)) est *invariant en grandeur et en signe*.

On vérifie aisément, en effet, que l'inversion d'écriture de la réaction d'électrode



à l'électrode Zn/Zn^{2+} implique un changement de signe simultanément pour l'affinité électrochimique et pour la charge réactionnelle, le quotient de ces deux quantités étant donc invariant en grandeur et en signe.

Ainsi que l'affinité électrochimique elle-même, ce quotient n'est différent de zéro que hors de l'équilibre. Dans le cas d'une électrode simple (voir III(17)), il sera appelé *tension électrochimique de l'électrode*.

Notons que, pour un état électrique de l'électrode correspondant à une réaction spontanée dans la direction de l'oxydation (dissolution d'un métal, formation d'un halogène ou d'un sel à partir de l'anion correspondant, etc.), la tension électrochimique est positive. Pour le même état chimique de l'électrode, mais pour un état électrique correspondant à une réaction spontanée dans la direction de la réduction (dépôt d'un métal, formation d'un anion à partir d'un halogène ou d'un sel, etc.), la tension électrochimique est négative.

(21) Si, pour un état chimique donné d'une électrode, on permute les membres de gauche et de droite de la réaction d'électrode, sans changer l'ordre de numérotation des phases, le quotient de l'affinité chimique de cette réaction d'électrode par la charge réactionnelle correspondante (telle qu'elle a été définie en III(9)) est invariant en grandeur et en signe.

Dans le cas d'une électrode simple (voir III(17)), ce quotient sera appelé *tension chimique de l'électrode*.

L'expression *tension chimique* est préférable à la désignation *force électromotrice* de l'électrode, laquelle serait néanmoins conforme à l'usage courant de cette appellation en thermodynamique électrochimique.

(22) On montre aisément que la *tension électrique réversible* ou *d'équilibre* d'une électrode simple est égale à moins la tension chimique de cette électrode.

Elle est donc aussi égale à moins l'affinité chimique de la réaction d'électrode divisée par la charge réactionnelle.

A l'équilibre la somme tension chimique + tension électrique est égale à zéro.

Hors de l'équilibre la tension électrique diffère en valeur absolue de la tension chimique. La somme tension chimique + tension électrique est alors égale à la tension électrochimique définie en III(20), maintenant différente de zéro.

Les diverses tensions définies plus haut expriment la tendance, soit d'origine électrochimique, soit d'origine chimique, soit d'origine électrique, qu'ont les charges positives à passer du métal (phase I) à la solution (phase II). L'équilibre, c'est à dire, l'absence d'un passage net de charges d'une phase à l'autre, a lieu lorsque les tendances chimique et électrique se compensent. La tension électrochimique est alors nulle, la tension chimique et la tension électrique étant égales en valeur absolue mais de signes contraires.

Représentons par $\tilde{\epsilon}^{I/II}$ la tension électrochimique entre la phase I et la phase II, par $\tilde{\epsilon}^{I/II}$ la tension chimique et par $g^{I/II}$ la tension électrique (ou tension Galvani). Nous avons en général:

$$\tilde{\epsilon}^{I/II} = \epsilon^{I/II} + g^{I/II}$$

avec:

$$\epsilon^{I/II} = A/zF \quad \text{et} \quad g^{I/II} = \varphi^I - \varphi^{II}$$

A l'équilibre électrochimique:

$$g_{\text{rév.}}^{I/II} = -\epsilon^{I/II} = -A/zF, \quad \tilde{\epsilon}_{\text{rév.}}^{I/II} = 0$$

D'où, en général:

$$\tilde{\epsilon}^{I/II} = g^{I/II} - g_{\text{rév.}}^{I/II}$$

(23) L'*effet chimique du courant* dû à un courant stationnaire traversant une interface est l'ensemble des modifications subies par les nombres de moles des constituants des régions terminales des phases situées de part et d'autre de l'interface*.

* LANGE, dans une publication intitulée "Über Phasenendumsätze an einfachen Elektroden" (*Z. Elektrochem.*, 61 (1957) 1301), considère l'*effet chimique du courant* défini en III(23) comme identique à l'*électrolyse* à une anode ou à une cathode, cette électrolyse étant régie par les lois de Faraday indépendamment de la nature de la contre-électrode, du signe de la tension électrique de la cellule correspondante et de la spontanéité ou non-spontanéité du fonctionnement de la cellule entière.

(24) Le nombre d'enrichissement d'un constituant de la région terminale d'une phase conductrice est l'accroissement du nombre de moles de ce constituant résultant du passage d'un faraday dans le sens indiqué par la numérotation des phases.

Considérons le constituant i des phases 1 et 2 traversées pendant le temps t par le courant stationnaire I (positif dans le sens 1-2, négatif dans le sens 2-1). L'accroissement du nombre de moles de i dans la région 1(2) de la phase 1 en contact avec la phase 2 est donné par

$$\Delta n_i^{1(2)} = \tau_i^{1(2)} t I / F$$

où $\tau_i^{1(2)}$ représente le nombre d'enrichissement de i dans la région 1(2). De même, dans la région 2(1) de la phase 2 en contact avec la phase 1, on a :

$$\Delta n_i^{2(1)} = \tau_i^{2(1)} t I / F$$

où $\tau_i^{2(1)}$ représente le nombre d'enrichissement de i dans la région 2(1).

(25) Considérons le cas où l'effet chimique du courant résulte d'une réaction d'électrode unique et de la migration des ions. Désignons par ν_i le coefficient stoechiométrique de i , constituant de la phase 1, dans la réaction d'électrode, par z le nombre de charges transportées par la réaction d'électrode, par θ_i^1 le nombre de transport de i dans la phase 1 et par z_i le nombre de faradays par mole de i . Nous avons :

$$\tau_i^{1(2)} = \nu_i^1 / z + \theta_i^1 / z_i$$

De même :

$$\tau_i^{2(1)} = \nu_i^2 / z - \theta_i^2 / z_i$$

IV. CELLULES GALVANIQUES

(1) Les *cellules galvaniques* sont des séries de phases conductrices en contact deux à deux, dont une au moins est un électrolyte ou une solution d'électrolytes, les interfaces correspondantes étant sièges d'effets chimiques lors du passage de courant (voir III(23)) et les phases terminales étant identiques l'une à l'autre aux points de vue chimique et physique, mais ayant en général des potentiels électriques intérieurs différents l'un de l'autre.

(2) On appelle *pôles* ou *bornes* les extrémités identiques (dans le sens défini en IV(1)) d'une cellule galvanique.

(3) (a) Une *pile* est une forme pratique de réalisation d'une cellule galvanique fonctionnant comme générateur d'énergie électrique. Le mot *pile* peut être considéré comme synonyme d'*élément*. Une *batterie* est un groupement de plusieurs piles ou éléments.

(b) Un *électrolyseur* est une forme pratique de réalisation d'une cellule galvanique fonctionnant comme consommateur d'énergie électrique.

Bien que l'ensemble des effets chimiques du courant dans une pile ou dans un électrolyseur doive toujours être regardé comme constituant une *électrolyse*, ces effets chimiques étant dans tous les cas conformes aux lois de Faraday, il existe, dans la pratique, une forte tendance à ne parler d'électrolyse qu'à propos des effets chimiques ayant lieu dans les électrolyseurs.*

(4) La *tension électrique d'une cellule galvanique* est la tension électrique d'un pôle

* La remarque faite à propos de la définition III(23) s'applique également à la définition IV(3) (b).

par rapport à l'autre. Elle est donc égale au potentiel électrique intérieur du premier pôle diminué de celui du second.

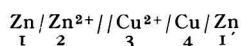
Les schémas des cellules galvaniques comprennent les différentes phases dans un ordre de succession déterminé. La tension est prise de la première phase à la dernière.

Si nous numérotons les phases de la manière suivante: $1/2/3 \dots /1'$, les phases 1 et 1' étant du même métal et constituant les pôles de la cellule galvanique, la tension électrique \mathcal{U} est égale à la différence $\varphi^1 - \varphi^{1'}$ entre les potentiels électriques intérieurs des phases 1 et 1':

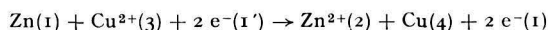
$$\mathcal{U} = \varphi^1 - \varphi^{1'}$$

(5) La *réaction de cellule* est la réaction électrochimique liée au passage du courant électrique dans la cellule, c'est à dire que cette réaction de cellule est la somme des réactions chimiques et des réactions d'électrodes associées à ce passage. Une réaction de cellule est donc une réaction chimique liée à un transport de charge à travers la cellule.

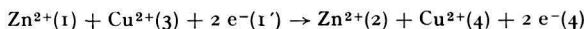
Considérons, par exemple, la pile Daniell et représentons-la par le schéma suivant:



La réaction de cellule correspondant au passage du courant dans le sens de la numérotation des phases est la suivante:

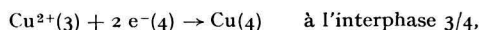
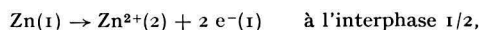


ou



Lorsque le courant électrique change de sens, la réaction de cellule avance de droite à gauche.

La réaction de cellule, dans sa première forme ci-dessus, peut être considérée comme la somme ou résultante des trois réactions suivantes:



Dans sa seconde forme la réaction de cellule peut être considérée comme la somme ou résultante des trois réactions suivantes:



Dans les deux formes on néglige de considérer les transferts d'ions à la jonction liquide.

Dans le fonctionnement en circuit fermé, ces réactions, dans leurs diverses formes ci-dessus, sont accompagnées du transfert d'électrons du pôle 1 au pôle 1' par le circuit extérieur.

(6) La *charge réactionnelle* de la réaction de cellule, ainsi que le *nombre de charges transportées* par la réaction de cellule, se définissent comme en III(9), les phases 1 et 2 devenant maintenant les pôles 1 et 1' de la cellule.

Dans le cas de la pile Daniell et de la réaction écrite dans le sens choisi en IV(5), la charge réactionnelle est +2 F et le nombre de charges transportées est +2.

(7) Dans le cas limite de cellules formées de successions de phases dans lesquelles les potentiels électrochimiques des constituants sont uniformes, l'*enthalpie libre électrochimique de la réaction de cellule* est égale à la somme des potentiels électrochimiques des produits de la réaction multipliés par leurs coefficients stoechiométriques diminuée des potentiels électrochimiques des réactifs multipliés par les valeurs absolues de leurs coefficients stoechiométriques. Dans cette opération les électrons des phases métalliques sont comptés parmi les réactifs et produits de la réaction.

Il en résulte que l'*enthalpie libre électrochimique* d'une réaction de cellule est égale à la somme des enthalpies libres électrochimiques des réactions dont la réaction de cellule est la résultante (voir III(10) et IV(5)).

L'*affinité électrochimique* d'une réaction de cellule, égale à la quantité précédente prise avec le signe moins, est aussi égale à la somme des affinités électrochimiques des réactions dont la réaction de cellule est la résultante (voir III(11) et IV(5)).

Dans le cas de l'exemple donné en IV(5) nous avons:

$$-\Delta\tilde{G} = \tilde{A} = -\sum_{\alpha} \sum_{\gamma} \nu_{\gamma}^{\alpha} \mu_{\gamma}^{\alpha} = \tilde{\mu}_{Zn}^1 + \tilde{\mu}_{Cu}^{3+2} + 2 \tilde{\mu}_{e^{-}}^1 - \tilde{\mu}_{Zn}^{2+2} - \tilde{\mu}_{Cu}^4 - 2 \tilde{\mu}_{e^{-}}^1$$

ou encore:

$$-\Delta\tilde{G} = \tilde{A} = \mu_{Zn}^1 + \tilde{\mu}_{Cu}^{3+2} - \tilde{\mu}_{Zn}^{2+2} - \mu_{Cu}^4 + 2 F (\psi^1 - \varphi^1),$$

où $\Delta\tilde{G}$ représente l'enthalpie libre électrochimique, \tilde{A} l'affinité électrochimique, μ un potentiel chimique, $\tilde{\mu}$ un potentiel électrochimique.

Lorsque les interphases 1/2, 3/4, 4/1' sont chacune à l'équilibre électrochimique, situation que nous considérons comme étant l'*équilibre électrochimique de la cellule*, $\Delta\tilde{G}$ et \tilde{A} sont nuls et nous avons, dans le cas de notre exemple, une tension électrique de cellule dite *réversible* donnée par

$$\mathcal{U}_{rév.} = (\varphi^1 - \varphi^{1'})_{rév.} = (\mu_{Zn}^{2+2} + \mu_{Cu}^4 - \mu_{Zn}^1 - \mu_{Cu}^{2+2})/2 F + \varphi^2 - \varphi^3$$

La tension électrique $\varphi^2 - \varphi^3$ dans la zone de diffusion du liquide 2 au liquide 3 peut parfois être estimée et retranchée de la valeur $\mathcal{U}_{rév.}$ de la formule ci-dessus. On peut aussi appréciablement diminuer la valeur absolue de cette tension électrique en intercalant, entre les deux phases liquides, une solution concentrée d'un électrolyte dont les ions ont sensiblement la même mobilité électrique, par exemple une solution saturée de chlorure de potassium. Dans le cas d'une cellule galvanique ne comportant qu'une phase liquide, le problème de la jonction liquide ne se pose évidemment pas.

(8) L'*enthalpie libre chimique de la réaction de cellule* est égale à la somme des potentiels chimiques des produits de la réaction multipliés par leurs coefficients stoechiométriques diminuée des potentiels chimiques des réactifs multipliés par les valeurs absolues de leurs coefficients stoechiométriques.

L'enthalpie libre chimique de la réaction de cellule est donc égale à l'enthalpie libre électrochimique de la réaction, abstraction faite de tous les termes de la forme coefficient stoechiométrique \times charge molaire \times potentiel électrique intérieur.

L'affinité chimique de la réaction de cellule, égale à la quantité précédente prise avec le signe moins, est donc égale à l'affinité électrochimique de cette réaction, abstraction faite de tous les termes de la forme coefficient stoechiométrique \times charge molaire \times potentiel électrique intérieur.

Dans le cas de l'exemple donné en IV(5) nous avons :

$$- \Delta G = A = \mu_{\text{Zn}}^1 + \mu_{\text{Cu}^{2+}}^3 - \mu_{\text{Zn}^{2+}}^2 - \mu_{\text{Cu}}^4$$

où ΔG représente l'enthalpie libre chimique, A l'affinité chimique.

A l'équilibre électrochimique, c'est à dire à courant nul, et négligeant la contribution $\varphi^2 - \varphi^3$ de la jonction liquide ou introduisant une correction adéquate, la tension électrique réversible considérée en IV(7) s'écrit :

$$\mathcal{U}_{\text{rév.}} = -A/zF \quad (\text{en général: } \mathcal{U}_{\text{rév.}} = -A/zF)$$

Puisque, en général :

$$\vec{A} = A + zF\mathcal{U},$$

c'est à dire :

$$A \text{ électrochimique} = A \text{ chimique} + A \text{ électrique},$$

on a, à l'équilibre :

$$\vec{A} = A + zF\mathcal{U}_{\text{rév.}} = 0$$

La tension électrique réversible d'une cellule galvanique est donc égale à moins l'affinité chimique de la réaction de cellule divisée par la charge réactionnelle. Remarquons que cette relation est valable quel que soit le sens dans lequel on écrit la réaction de cellule : l'inversion de ce sens correspond à un changement de signe à la fois pour l'affinité chimique et pour la charge réactionnelle.

L'affinité électrochimique nulle correspondant au cas de l'équilibre électrochimique résulte de la compensation de l'affinité chimique par l'affinité électrique ou produit de la charge réactionnelle par la tension électrique réversible de la cellule.

Hors de l'équilibre, c'est à dire avec passage de courant, l'affinité électrochimique est égale à la somme de l'affinité chimique et du produit de la charge réactionnelle par la tension électrique de la cellule.

Dans les cellules dont les phases chimiquement homogènes sont sièges de chutes ohmiques, l'affinité électrochimique calculée par la relation

$$\vec{A} = A + zF\mathcal{U}$$

n'est plus égale à la somme des affinités électrochimiques des réactions qui ont lieu aux interphases. Elle est maintenant égale à cette somme augmentée du produit de la charge réactionnelle par la somme des tensions ohmiques s'établissant de la première à la seconde face de chaque phase.

(9) Ainsi qu'il a été fait en III(20) pour le cas d'une réaction d'électrode, nous

appellerons le quotient de l'affinité électrochimique de la réaction de cellule par la charge réactionnelle *tension électrochimique* de la cellule.

Le signe de la tension électrochimique n'est pas modifié si on inverse le sens d'écriture de la réaction de cellule. Au contraire, ce signe s'inverse si l'on inverse l'ordre de succession des phases.

Dans le cas du schéma de la pile Daniell choisi en IV(5) la tension électrochimique est positive (sauf si le rapport des concentrations $\text{Cu}^{2+}/\text{Zn}^{2+}$ est extrêmement petit). Dans le cas du schéma opposé (Cu à gauche, Zn à droite), la tension électrochimique serait négative. On voit donc qu'une tension électrochimique positive représente l'action combinée des forces chimiques et des forces électriques tendant à faire circuler, à l'intérieur de la cellule, les charges positives dans le sens 1/2/3. . . 1' de la numérotation des phases. A l'équilibre électrochimique les forces chimiques et les forces électriques s'équilibrent et la tension électrochimique est nulle.

(10) Ainsi qu'il a été fait en III(21) pour le cas d'une réaction d'électrode, nous appellerons le quotient de l'affinité chimique de la réaction de cellule par la charge réactionnelle *tension chimique* de la cellule.

Le signe de la tension chimique n'est pas modifié si on inverse le sens d'écriture de la réaction de cellule. Au contraire, ce signe s'inverse si l'on inverse l'ordre de succession des phases.

Cette tension chimique de la cellule est identique à la grandeur couramment appelée *force électromotrice* de la cellule dans la littérature de la chimie physique, de la thermodynamique et de l'électrochimie. Nous considérons l'appellation *tension chimique* de la cellule comme nettement préférable.

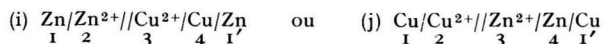
Dans le cas du schéma de la pile Daniell choisi en IV(5) la tension chimique est positive (sauf si le rapport des concentrations $\text{Cu}^{2+}/\text{Zn}^{2+}$ est extrêmement petit). Dans le cas du schéma opposé (Cu à gauche, Zn à droite), la tension chimique serait négative. On voit donc qu'une tension chimique (ou force électromotrice) positive représente l'action des forces non-électriques, c'est à dire chimiques, tendant à faire circuler, à l'intérieur de la cellule, les charges positives dans le sens 1/2/3. . . 1' de la numérotation des phases.

(11) Il résulte de IV(8) que la *tension électrique* de la cellule est égale à la tension électrochimique diminuée de la tension chimique.

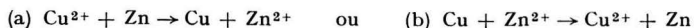
A l'équilibre électrochimique la tension électrique est égale à moins la tension chimique.

Dans le cas de la pile Daniell et du schéma choisi en IV(5), la tension électrique est négative (sauf si le rapport des concentrations $\text{Cu}^{2+}/\text{Zn}^{2+}$ est extrêmement petit). Dans le cas du schéma opposé (Cu à gauche, Zn à droite), la tension électrique serait positive. On peut considérer qu'une tension électrique positive implique l'existence de forces chimiques tendant à faire circuler, à l'intérieur de la cellule, les charges positives dans le sens inverse de la numérotation des phases, soit 1'/. . . /3/2/1. Le mouvement réel des charges est dû à l'action combinée des forces électriques et des forces chimiques, c'est à dire à l'action de la tension électrochimique.

(12) Reprenons le cas de la pile Daniell. Elle peut être représentée par l'un ou l'autre des deux schémas suivants:



La réaction de cellule peut, en abrégé, s'écrire sous l'une ou l'autre des deux formes suivantes:



Les nombres de charges transportées sont :

$$z_{ia} = +2, \quad z_{ja} = -2, \quad z_{ib} = -2, \quad z_{jb} = +2$$

Les affinités chimiques et les enthalpies libres chimiques des réactions a et b sont reliées par les relations suivantes :

$$A_a = -\Delta G_a = -A_b = +\Delta G_b$$

La tension chimique (ou force électromotrice) correspondant au schéma i est donnée par les quatre rapports :

$$\mathcal{E}_i = (+A_a)/(+2 F) = (-\Delta G_a)/(+2 F) = (+A_b)/(-2 F) = (-\Delta G_b)/(-2 F)$$

tandis que la tension électrique réversible correspondant au schéma i est donnée par les quatre rapports :

$$\mathcal{U}_{i,rév.} = (-A_a)/(+2 F) = (+\Delta G_a)/(+2 F) = (-A_b)/(-2 F) = (+\Delta G_b)/(-2 F)$$

La tension chimique (ou force électromotrice) correspondant au schéma j est donnée par les quatre rapports :

$$\mathcal{E}_j = (+A_a)/(-2 F) = (-\Delta G_a)/(-2 F) = (+A_b)/(+2 F) = (-\Delta G_b)/(+2 F)$$

tandis que la tension électrique réversible correspondant au schéma j est donnée par les quatre rapports :

$$\mathcal{U}_{j,rév.} = (-A_a)/(-2 F) = (+\Delta G_a)/(-2 F) = (-A_b)/(+2 F) = (+\Delta G_b)/(+2 F)$$

On vérifie donc bien que

$$\mathcal{U}_{i,rév.} + \mathcal{E}_i = 0 \quad \text{et} \quad \mathcal{U}_{j,rév.} + \mathcal{E}_j = 0$$

Hors de l'équilibre, mais à température, pression et composition chimique données, la tension chimique (ou forces électromotrice) conserve la même valeur qu'à l'équilibre, tandis que la tension électrique s'écarte de sa valeur réversible ou d'équilibre dans une direction dépendant du sens du courant qui traverse alors la cellule. Si le sens du courant est celui correspondant à la direction spontanée de la réaction de cellule (direction déterminée par le signe de l'affinité purement chimique), la valeur absolue de la tension électrique est plus petite que la valeur absolue de la tension électrique réversible. Si le sens du courant est celui correspondant à la direction non-spontanée de la réaction de cellule, la valeur absolue de la tension électrique réversible.

Les relations ci-dessus entre la tension électrique réversible ou la tension chimique (ou force électromotrice) d'une cellule galvanique, d'une part, et l'affinité chimique ou l'enthalpie libre chimique de la réaction de cellule, d'autre part, satisfont au desideratum électrochimique selon lequel on doit pouvoir associer, à un schéma déterminé d'une cellule galvanique, deux directions de la réaction de cellule correspondant aux deux directions possibles du courant électrique.

Il est souvent considéré comme pratique, une fois le pôle positif de la cellule expressément désigné, de n'employer que la valeur arithmétique de la tension chimique (ou force électromotrice) de la cellule, ou, ce qui revient alors au même, celle de sa tension électrique réversible.

(13) On démontre aisément que la tension électrique $\mathcal{U} = \varphi^1 - \varphi^{1'}$ d'une cellule galvanique 1/2/3/4/1', dont la phase métallique 4 est différente des phases métalliques chimiquement identiques 1 et 1', est égale au potentiel électrochimique de l'électron dans la phase 4 diminué du potentiel électrochimique de l'électron dans la phase 1 et divisé par un faraday.

On a, en effet :

$$\mathcal{U} = \varphi^1 - \varphi^{1'} = (\tilde{\mu}_e^4 - \tilde{\mu}_e^1)/F$$

puisque :

$$\mu_e^1 = \mu_e^{1'}$$

Au contact intermétallique 4/1' il y a toujours équilibre électrochimique pour le transfert de l'électron et on a donc :

$$\tilde{\mu}_e^{1'} = \tilde{\mu}_e^4$$

Il en résulte que :

$$\mathcal{U} = (\tilde{\mu}_e^4 - \tilde{\mu}_e^{1'}) / F$$

Considérons maintenant le passage de l'électron de 4 à 1 par l'intermédiaire de 1' et d'un fil métallique reliant 1' à 1. Comme en III(20), nous pouvons définir ici une *tension électrochimique* égale au quotient de l'affinité électrochimique de ce transfert d'électrons par la charge réactionnelle, égale ici à moins un faraday. Cette tension électrochimique est égale à moins la tension électrique \mathcal{U} de la cellule galvanique :

$$\mathcal{E} = (\tilde{\mu}_e^4 - \tilde{\mu}_e^{1'}) / (-F) = -\mathcal{U}$$

Si la tension électrochimique \mathcal{E} est positive, les électrons passeront de 1 à 4 via le fil et 1'. En d'autres termes, le courant positif passera de 4 à 1' via 1' et le fil. L'inverse sera le cas lorsque la tension électrochimique \mathcal{E} sera négative.

(14) La *tension électrique relative d'une électrode* est, déduction faite des tensions des jonctions liquides, s'il y en a, la tension électrique d'une cellule galvanique comprenant successivement : le métal et la solution de l'électrode étudiée, la solution et le métal d'une électrode de référence, enfin un pôle terminal de même métal que celui de l'électrode étudiée.

Une telle cellule galvanique est appelée *cellule tensiométrique*.

La tension électrique relative est rigoureusement accessible dans le cas exceptionnel où l'électrode de référence comporte la même solution d'électrolytes que l'électrode envisagée. Elle est alors égale à la tension électrique de la cellule définie par la succession : métal de l'électrode étudiée/solution d'électrolytes commune aux deux électrodes/métal de l'électrode de référence/métal identique à celui de l'électrode étudiée.

Quand l'électrode de référence ne comporte pas la même solution d'électrolytes que l'électrode envisagée, on peut obtenir une valeur approximative, à quelques millivolts près, de la tension électrique relative en intercalant, entre les deux phases liquides, comme cela a déjà été mentionné en IV(7), une solution saturée de chlorure de potassium.

(15) (a) On appelle *solution diluée idéale* une solution diluée telle qu'à température et pression totale constantes, le potentiel chimique de chaque constituant dissous varie linéairement avec le logarithme naturel de sa molarité (ou de sa molalité, ou de son titre molaire) avec un coefficient angulaire égal au produit de la constante molaire des gaz parfaits par la température absolue. On a donc, en fonction par exemple de la molalité m_i du constituant dissous i :

$$\mu_i = \mu_i^\circ + RT \ln m_i$$

où μ_i° est une fonction de la température et de la pression seulement appelée *potentiel chimique standard* du constituant dissous i .

En électrochimie on n'emploie qu'exceptionnellement les titres molaires des corps dissous dans les phases condensées et on emploie leurs molalités plus généralement que leurs molarités*.

Dans le cas des électrolytes dissous, le domaine d'idéalité peut perdre sa signification expérimentale aux dilutions accessibles. Nous verrons ci-après comment les potentiels chimiques standard se définissent dans ce cas.

* Voir note à la page suivante.

(b) Le potentiel chimique du solvant, constituant 1, d'une solution idéale est toujours donné par:

$$\mu_1 = \mu_1^\circ + RT \ln x_1$$

où x_1 représente le titre molaire du solvant et μ_1° son potentiel chimique standard, numériquement égal au potentiel chimique du corps pur correspondant.

(c) Le potentiel chimique d'un constituant j d'un mélange gazeux idéal (et, pratiquement, celui d'un constituant j d'un mélange gazeux sous pression totale suffisamment basse) est de même toujours donné par:

$$\mu_j = \mu_j^\circ + RT \ln x_j$$

où x_j représente le titre molaire du gaz j et μ_j° son potentiel chimique standard, numériquement égal au potentiel chimique du gaz j à l'état pur, à la même température que celle du mélange et à une pression égale à la pression totale du mélange, le gaz j pur étant alors assimilable à un gaz parfait.

Dans beaucoup de cas, cette assimilation est possible jusqu'au voisinage d'une atmosphère; aux pressions plus élevées, le potentiel chimique standard s'obtient en ajoutant le terme $RT \ln p$ au potentiel chimique standard pour une atmosphère.

(16) (a) L'activité a_i d'un constituant i d'une solution condensée est l'exponentielle du quotient par RT de son potentiel chimique diminué de son potentiel chimique standard:

$$a_i = \exp(\mu_i - \mu_i^\circ) / RT$$

Il résulte de cette formule que le potentiel chimique s'écrit dans tous les cas sous la forme:

$$\mu_i = \mu_i^\circ + RT \ln a_i$$

(b) Pour un constituant i d'une solution idéale, l'activité s'identifie numériquement, selon le potentiel chimique standard choisi, à la molalité, à la molarité ou autre titre molaire.

(17) (a) Dans le cas des électrolytes, on conserve la forme du potentiel chimique

$$\mu_i = \mu_i^\circ + RT \ln a_i$$

sans définir *a priori* la valeur de μ_i° , laquelle reste cependant fonction de la température et de la pression seulement.

* Considérons une quantité de solution contenant 1000 g de solvant 1 de poids moléculaire M_1 et $m_2, \dots, m_i, m_j, \dots, m_s$ moles des corps dissous 2, ..., i, j, \dots, s . La molalité du corps dissous i est m_i . Son titre molaire x_i est donné par:

$$x_i = m_i / (\sum_2^s m_j + 1000/M_1)$$

celui du solvant est donné par:

$$x_1 = (1000/M_1) / (\sum_2^s m_j + 1000/M_1)$$

Si le volume de cette quantité de solution est V litres, le quotient m_i/V est la molarité C_i de i dans cette solution.

Lorsqu'on emploie les molalités, on pose :

$$a_i = m_i \gamma_i$$

où γ_i est appelé *coefficient d'activité* du constituant i .

Le potentiel chimique s'écrit alors :

$$\mu_i = \mu_i^\circ + RT \ln (m_i \gamma_i)$$

Le potentiel chimique standard μ_i° est alors choisi de telle manière que γ_i tende vers l'unité lorsque m_i tend vers zéro.

(b) L'activité d'un ion dissous ne peut pas être obtenue expérimentalement ; par contre, l'activité moyenne des deux ions A et B d'un électrolyte $A_{\nu_+} B_{\nu_-}$, c'est à dire la moyenne géométrique pondérée

$$a_{\pm} = (a_+^{\nu_+} a_-^{\nu_-})^{1/(\nu_+ + \nu_-)}$$

peut être obtenue expérimentalement.

(c) Le coefficient d'activité d'un ion dissous ne peut pas être obtenu expérimentalement. Par contre, le coefficient d'activité moyen des deux ions A et B d'un électrolyte $A_{\nu_+} B_{\nu_-}$, c'est à dire la moyenne géométrique pondérée

$$\gamma_{\pm} = (\gamma_+^{\nu_+} \gamma_-^{\nu_-})^{1/(\nu_+ + \nu_-)}$$

peut être obtenue expérimentalement.

(18) On appelle *tension électrique standard* d'une électrode simple, à une température et une pression données, la valeur qu'aurait sa tension électrique relative pour un état d'équilibre électrochimique, lequel sera souvent fictif, tel que le potentiel chimique de chaque constituant participant à la réaction d'électrode soit numériquement égal au potentiel chimique standard de ce constituant à la température et la pression données.

L'électrode de référence de la cellule tensiométrique se trouvant elle-même dans un tel état, la tension électrique standard \mathcal{Q}° et la tension chimique standard \mathcal{E}° correspondante de l'électrode étudiée sont données par :

$$\mathcal{Q}^\circ = -\mathcal{E}^\circ = \left(\sum_{\gamma} \nu_{\gamma} \mu_{\gamma}^\circ \right) / zF = -A^\circ / zF = \Delta G^\circ / zF$$

la somme $\sum_{\gamma} \nu_{\gamma} \mu_{\gamma}^\circ$ étant étendue à tous les réactifs et produits de la réaction de la cellule tensiométrique, A° étant l'*affinité chimique standard* et ΔG° l'*enthalpie libre chimique standard* de cette réaction de cellule.

Les valeurs numériques des tensions électriques standard dépendent du choix fait, pour les corps dissous, entre molalités, molarités ou titres molaires et également du choix de l'électrode de référence. Notons à ce propos que l'écart de tension électrique entre électrodes analogues dont les solutions seraient l'une de molalité m et l'autre de molarité m est de l'ordre du dixième de millivolt dans le cas de solutions aqueuses diluées.

Les tensions électriques standard permettent de situer les diverses électrodes dans la *série des tensions*.

(19) L'électrode de référence ordinairement choisie est l'*électrode standard à hydro-*

gène à une atmosphère, c'est à dire une électrode réversible à hydrogène dont les ions hydrogène ont une activité égale à l'unité et l'hydrogène gazeux a une pression d'une atmosphère.

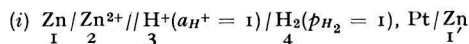
Il en résulte que la tension électrique standard de l'électrode à hydrogène est égale à zéro à toute température, mais c'est pour la température de 25° que les tables de tensions électriques standard sont le plus souvent établies.

La tension électrique standard d'une autre électrode réversible quelconque peut être déterminée, avec une précision atteignant dans certains cas le centième de millivolt, au moyen d'une cellule à un seul compartiment liquide accouplant à l'électrode envisagée soit une électrode à hydrogène, soit une électrode réversible différente déjà étudiée.

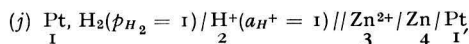
La tension électrique standard est en effet égale à une combinaison linéaire de potentiels chimiques standard divisée par la charge réactionnelle. Sa valeur s'obtient de manière rigoureuse par une extrapolation de certaines valeurs expérimentales correspondantes jusqu'à dilution infinie.

(20) Lorsque l'électrode de référence est l'électrode standard à hydrogène, la *tension électrique relative d'électrode* définie en VI(14) est appelée également *potentiel relatif d'électrode*, ou, plus brièvement, *potentiel d'électrode*. Dans le cas de l'équilibre, cette grandeur est identique à celle définie sous ce nom par l'Union Internationale de Chimie Pure et Appliquée (I.U.P.A.C.) dans ses recommandations de Stockholm (1953, texte remanié par la Commission d'Electrochimie à Madrid, 1956, et à Paris, 1957).

Dans le cas de l'électrode Zn/Zn^{2+} , par exemple, la *tension électrique relative* est la tension de la cellule



tandis que le *potentiel d'électrode* est défini dans les recommandations I.U.P.A.C. comme étant la force électromotrice de la cellule



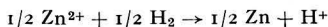
Il est bien clair qu'à l'équilibre électrochimique ces deux quantités sont identiques:

$$\mathcal{U}_{i,rév.} = \mathcal{E}_j$$

Hors de l'équilibre la tension électrique et le potentiel d'électrode restent identiques l'un à l'autre, mais ne sont plus égaux à \mathcal{E}_j .

Notre définition de la tension électrique relative implique automatiquement l'usage des signes dits "européens" (tensions électriques nobles positives, égales, à l'équilibre, aux potentiels dits "de réduction"). Le montage avec premier pôle attaché à l'électrode de référence et second pôle constitué par le métal de l'électrode étudiée, qui est opposé à celui décrit en IV(14), conduirait automatiquement à l'usage des signes dits "américains" (tensions électriques nobles négatives, égales, à l'équilibre, aux potentiels dits "d'oxydation").

(21) Les valeurs réversibles ou d'équilibre des tensions électriques relatives avec signes dits "européens" sont égales aux affinités chimiques des réactions écrites dans le sens de la réduction par $1/2 H_2$ à $p_{H_2} = 1$ atmosphère devenant H^+ à $a_{H^+} = 1$, divisées par un faraday:

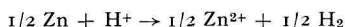


Dans la cellule *i* on a :

$$\mathcal{U}_{i,rév.} = A_{réd.}/F = \mathcal{U}_{rév., eur.}$$

Les quantités communément appelées "potentiels de réduction" sont donc des *affinités de réduction* rapportées à l'unité de charge prise en valeur absolue. Dans le système d'unités pratiques elles sont exprimées en volts.

De même, les valeurs réversibles ou d'équilibre des tensions électriques relatives avec signes dits "américains" sont égales aux affinités chimiques des réactions écrites dans le sens de l'oxydation par H^+ à $a_{H^+} = 1$ devenant $1/2 H_2$ à $p_{H_2} = 1$ atmosphère, divisées par un faraday :



Dans la cellule *j* on a :

$$\mathcal{U}_{j,rév.} = A_{oxyd.}/F = \mathcal{U}_{rév., amér.}$$

Les quantités communément appelées "potentiels d'oxydation" sont donc des *affinités d'oxydation* rapportées à l'unité de charge prise en valeur absolue. Dans le système d'unités pratiques elles sont exprimées en volts.

(22) Le coefficient de température $d\mathcal{U}/dT$ de la tension électrique d'une cellule isotherme est la limite, pour T_2 tendant vers T_1 , du rapport

$$(\mathcal{U}_2 - \mathcal{U}_1)/(T_2 - T_1)$$

où \mathcal{U}_2 et \mathcal{U}_1 sont les tensions électriques de deux cellules isothermes (de même composition) aux températures T_2 et T_1 , respectivement.

V. SYSTÈMES NON-ISOTHERMES

Les quelques définitions présentées ici ne sont qu'une introduction à l'étude des systèmes électrochimiques non-isothermes. Cette partie du rapport comprendra ultérieurement des définitions se rapportant aux cellules galvaniques non-isothermes.

(1) Un *thermocouple* est un système électrochimique à trois phases $1/2/1'$ constitué de deux métaux 1 et 2, $1'$ étant du même métal que 1, et dont les régions interphases $1/2$ et $2/1'$ sont à des températures différentes T et T' , la phase 1 et la région terminale de $1'$ vers la droite étant à la même température T que la région interphase $1/2$.

Dans un tel système les effets chimiques du courant aux interphases sont nuls.

(2) La *tension thermoélectrique* de ce thermocouple ($1/2$) est donnée, à courant nul, par

$$\mathcal{U} = -\Delta\varphi = \varphi^1 - \varphi^{1'}$$

où φ^1 est le potentiel électrique intérieur de la phase 1 et $\varphi^{1'}$ est celui de la région terminale de droite de la phase $1'$.

Cette tension \mathcal{U} est une fonction de la nature des métaux 1 et 2 et, pour une valeur donnée T' de la température de la source froide, de l'écart $T - T'$ des températures.

Par convention, la *tension thermoélectrique* $\mathcal{U}(1/2)$ d'un couple de métaux ($1/2$) est celle que l'on mesure à l'aide du thermocouple décrit ci-dessus lorsque l'interface $1/2$ est la soudure chaude et l'interface $2/1'$ la soudure froide.

(3) Dans un conducteur métallique homogène soumis à un gradient de température, il existe un gradient de potentiel électrique. Nous ne considérerons ici que le cas où ces gradients sont parallèles.

La *tension thermoélectrique homogène* entre un point A et un point B au sein du même métal \mathfrak{r} est

$$\mathscr{U} = \varphi_{A^1} - \varphi_{B^1} = [(\varphi_{B^1} - \varphi_{A^1}) / (T_B - T_A)] (T_A - T_B)$$

Le *pouvoir thermoélectrique homogène* du métal \mathfrak{r} est défini par la limite du rapport

$$(\varphi_{B^1} - \varphi_{A^1}) / (T_B - T_A)$$

lorsque les deux points deviennent infiniment voisins. On le désignera par $d\varphi^1/dT$. Lorsque T_B est voisin de T_A , la *tension thermoélectrique homogène* peut s'écrire :

$$\mathscr{U} = \varphi_{A^1} - \varphi_{B^1} = (d\varphi^1/dT) (T_A - T_B)$$

(4) La tension électrique du thermocouple défini en $V(\mathfrak{r})$ est la somme de la tension Galvani $g^{1/2}$ à l'interface $\mathfrak{r}/2$, de la tension thermoélectrique homogène d'une extrémité à l'autre de la phase \mathfrak{z} dont la température n'est pas uniforme, de la tension Galvani $g^{2/1'}$ et de la tension thermoélectrique homogène sur la longueur de la phase \mathfrak{r}' .

Lorsque l'écart de température $T - T'$ devient infiniment petit, on remplace T par $T' + dT$. La tension du thermocouple est alors infiniment petite et s'écrit, d'après ce qui précède :

$$d\mathscr{U}(\mathfrak{r}/2) = d(\varphi^1 - \varphi^{1'}) = g^{1/2}(\text{à } T' + dT) + (d\varphi^2/dT)dT + g^{2/1'}(\text{à } T') - (d\varphi^1/dT)dT$$

(5) Le *pouvoir thermoélectrique d'un couple de métaux* est la limite du rapport de la tension thermoélectrique à la différence de température $T - T'$ qui la cause. On le désigne par

$$u(\mathfrak{r}/2) = d\mathscr{U}(\mathfrak{r}/2)/dT$$

où dT a la même signification que dans la formule de la définition $V(4)$.

Comme $g^{2/1'}(\text{à } T') = -g^{1/2}(\text{à } T')$, on a :

$$u(\mathfrak{r}/2) = dg^{1/2}/dT + d\varphi^2/dT - d\varphi^1/dT$$

(6) (a) Après déduction de la chaleur dégagée par l'effet Joule, la *chaleur de Thomson* est la chaleur dégagée par la surface extérieure d'un fil métallique homogène soumis à un gradient de température et parcouru par un courant électrique.

Un changement de la direction du courant par rapport à celle du gradient de température entraîne un changement de signe de cette chaleur.

(b) Le *coefficient de Thomson* σ est la chaleur de Thomson dégagée par le passage de \mathfrak{r}° coulomb dans une longueur de fil correspondant à un abaissement de température de \mathfrak{r}° , le courant allant de l'extrémité chaude à l'extrémité froide de la longueur de fil considérée.

(7) Le pouvoir thermoélectrique $u(\mathfrak{r}/2)$ d'un couple de métaux (voir $V(5)$), le coefficient de Peltier $\pi(\mathfrak{r}/2)$ relatif à leur interface (voir $\text{III}(\mathfrak{r}6)$ (b)) et leurs coefficients de Thomson respectifs σ^1 et σ^2 (voir $V(6)$ (b)) sont liés par les *deux relations de Thomson* :

$$u(\mathfrak{r}/2) = \pi(\mathfrak{r}/2)/T$$

$$(\sigma^1 - \sigma^2)/T = \partial u(\mathfrak{r}/2)/\partial T.$$

DIE WIRKUNG VON TETRAÄTHYLAMMONIUMSALZEN AUF DEN KATALYTISCHEN STROM ORGANISCHER STOFFE IN KOBALTFREIEN SYSTEMEN

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Auf Grund unserer früheren Untersuchungen¹ zogen wir die Schlussfolgerung, dass die keine Pufferwirkung ausübenden in Lösung vorhandenen starken Elektrolyte den katalytischen Strom vermindern, bzw. in genügend hoher Konzentration auch vollkommen aufheben. Diese Erscheinung kann damit erklärt werden, dass die an den Elektrodenoberflächen auftretenden stationären Gleichgewichtskonzentrationen, die die Grösse des katalytischen Stromes determinieren, durch fremde Elektrolyte dadurch verändert werden, dass diese die Konzentration der beiden Hauptteilnehmer des Prozess, nämlich des Puffers und des Katalysators, in der Oberflächenezone der Elektrode vermindern.

In den weiteren Untersuchungen stellten wir fest, dass die Zusammenhänge in Gegenwart von Tetraäthylammoniumsalzen komplizierter sind als beim oben umrissenen einfachen Fall. Die Höhe der katalytischen Stufe nimmt mit der Erhöhung der Konzentration des quaternären Ammoniumsalzes zuerst zu, über einer bestimmten Salzkonzentration bewirkt jedoch die Erhöhung der Konzentration des Tetraäthylammoniumsalzes eine Abnahme des katalytischen Stromes. Die nachstehend zu beschreibenden Versuche wurden zwecks experimenteller Begründung der Erklärung dieser Erscheinung durchgeführt.

EXPERIMENTELLE METHODIK

Zu den Untersuchungen wurde der Polarograph „Radelkisz“, Type 7-77-4 verwendet. Die Daten der Kapillare waren folgende: Auslaufgeschwindigkeit bei 85.0 cm Quecksilberhöhe: 0.221 g Hg/Min, in destilliertem Wasser gemessen. Tropfzeit bei obigen Bedingungen: 2.38 sec. Zur Kontrolle des pH-Wertes der Pufferlösungen wurde ein „Orion K.T.S.“ pH-Messgerät (Type: 2518/S) mit einer Kette gesättigter Kalomel-elektrode-Glaselektrode verwendet.

Chemikalien

1/15 M Phosphatpuffer (hergestellt aus analytisch reinem KH_2PO_4 „Merck“ und Na_2HPO_4 „Mallincrodt“, nach Sörensen; pH-Wert gemessen).

Britton-Robinsonscher Puffer 0.04 M (hergestellt aus analytisch reinen Chemikalien; mit nachfolgender pH-Messung).

Nikotinsäureamid, reinst
 Methylenblau „zur Analyse“ „Merck“
 Tetraäthylammoniumbromid (zweimal umkristallisiert).

EXPERIMENTELLE ERGEBNISSE

Die Messungen wurden mit zwei Katalysatoren: Methylenblau und Nikotinsäureamid durchgeführt. Die Anwendung dieser beiden Verbindungen als experimentelle Modelle war begründet durch die Tatsache, dass die polarographische Dissoziationskonstante beider Substanzen nach Angaben der einschlägigen Fachliteratur aus mehreren Gesichtspunkten untersucht wurde und sich auch im Laufe unserer späteren Berechnungen als gut verwendbar erwies^{2,3}.

Die Form der in Abhängigkeit von der Konzentration des Tetraäthylammoniumsalzes veränderlichen Stromstärkefunktion wird durch die Wasserstoffionenkonzentration beeinflusst. Wir bestimmten diese Wirkung, indem wir die Abhängigkeit des katalytischen Stromes von der Konzentration des Tetraäthylammoniumbromids bei mehreren pH-Werten feststellten. In den Tabellen I und II sind aus der Reihe der erhaltenen Ergebnisse die zu niedrigen Konzentrationen des Tetraäthylammoniumsalzes gehörenden Werte dieser Funktionen zusammengestellt.

TABELLE I

pH 6.40		pH 6.85		pH 7.62	
Tetraäthylammoniumbromid (mol/Lit.)	Katalytischer Strom (μA)	Tetraäthylammoniumbromid (mol/Lit.)	Katalytischer Strom (μA)	Tetraäthylammoniumbromid (mol/Lit.)	Katalytischer Strom (μA)
0.00	76.8	0.00	23.4	0.00	1.08
$1.38 \cdot 10^{-3}$	126	$1.38 \cdot 10^{-3}$	43.8	$6.92 \cdot 10^{-4}$	1.89
$3.68 \cdot 10^{-3}$	160	$3.50 \cdot 10^{-3}$	70.4	$2.2 \cdot 10^{-3}$	5.04
$6.92 \cdot 10^{-3}$	216	$4.45 \cdot 10^{-3}$	91.0	$2.77 \cdot 10^{-3}$	5.40
$1.43 \cdot 10^{-2}$	261	$1.19 \cdot 10^{-2}$	132	$4.58 \cdot 10^{-3}$	8.60

Die in Tabelle I gezeigten Daten sind die zusammengehörigen Wertpaare der bei einer Methylenblau-Konzentration von $9.1 \cdot 10^{-6}$ mol/Liter aufgenommenen Funktion bei 3 verschiedenen pH-Werten. Als Puffer diente der Phosphatpuffer der Konzentration von 1/15 mol/Liter. Die Höhe der Quecksilbersäule betrug 85.0 cm.

TABELLE II

pH 5.25		pH 5.40	
TEA Br-Konz. (mol/Lit.)	Katalytischer Strom (μA)	TEA Br-Konz. (mol/Lit.)	Katalytischer Strom (μA)
0.00	81.0	0.00	58.0
$1.19 \cdot 10^{-3}$	85.5	$1.19 \cdot 10^{-3}$	63
$2.38 \cdot 10^{-3}$	90.0	$2.46 \cdot 10^{-3}$	67
$4.24 \cdot 10^{-3}$	91.5	$6.03 \cdot 10^{-3}$	70
$1.42 \cdot 10^{-2}$	82.5	$1.24 \cdot 10^{-2}$	68

Tabelle II zeigt die bei einer Nikotinsäureamid-Konzentration von $9,1 \cdot 10^{-5}$ mol/Liter gemessenen Werte des katalytischen Stromes bei zunehmenden TEABr-Konzentrationen. Die in der Tabelle angegebenen beiden pH-Werte wurden mit Britton-Robinsonschem Puffer hergestellt. Die Höhe der Quecksilbersäule betrug 85,0 cm.

Für die nachstehend zu beschreibenden theoretischen Zwecke konnte beim Nikotinsäureamid nur eine viel engere TEABr-Konzentrationszone verwendet werden, da der aufsteigende Abschnitt der Funktion infolge der hohen Konzentration des Britton-Robinsonschen Puffers bereits bei geringer Erhöhung der Salzkonzentration nach Durchlaufen eines Maximums abzunehmen beginnt.

DISKUSSION DER ERGEBNISSE

Die den katalytischen Strom verstärkende Wirkung der Tetraäthylammoniumsalze kann in jenes Schema, das man bei der eingehenden Untersuchung der Effekte jener Faktoren, die den katalytischen Strom beeinflussen erhält, nicht ohne weiteres eingliedert werden. Der Grossteil der fremden Elektrolyte vermindert den katalytischen Effekt. In der zur Erklärung dieser Erscheinungen aufgestellten Arbeitshypothese nahmen wir an, dass aus den Tetraäthylammonium-Ionen im Kraftfeld in der Umgebung der Grenzfläche der Elektrode je ein Proton abgespalten wird, das den pH-Wert an der Oberfläche der Elektrode verschiebt. Bekanntlich verursacht die Abnahme des pH-Wertes, bei übrigens konstanten Parametern, eine Erhöhung der katalytischen Stufen. Die Ursache hierfür liegt darin, dass sich der zur Ausbildung der aktiven Form des Katalysators notwendige protolytische Prozess in der Umgebung der Elektrode bei Abnahme des pH-Wertes mit grösserer Intensität abspielt. Diese Erklärung gibt Antwort auf die Frage, warum der katalytische Strom bei Erhöhung der Konzentration des Tetraäthylammoniumsalzes zunimmt. Wir bewiesen die Richtigkeit unserer Annahme auch auf rechnerischem Wege.

Für die Bildung der aktiven Form des Katalysators gilt folgendes Proton-Assoziationsgleichgewicht:



B ist hier die inaktive (Brönstedsche Base) und BH^+ die aktive Form des Katalysators. Schreibt man das Massenwirkungsgesetz für das Dissoziationsgleichgewicht auf, so erhält man den Ausdruck:

$$K_a = \frac{(1 - \alpha)C_H}{\alpha} \quad (2)$$

in diesem bedeutet α den Dissoziationsgrad der als Brönstedsche Säure vorhandenen aktiven Form, mit dem der katalytische Strom proportional ist, C_H ist die aktuelle Wasserstoffionenkonzentration und K_a die Konstante des obigen Gleichgewichts.

In logarithmischer Form lautet die Gleichung (2):

$$\log K_a = \log (1 - \alpha) + \log C_H - \log \alpha \quad (3)$$

und hieraus $-\log C_H$, das dem pH-Wert gleich ist:

$$-\log C_H = \text{pH} = -\log K_a + \log (1 - \alpha) - \log \alpha \quad (4)$$

Die Ableitung dieser Funktion nach α :

$$\frac{dpH}{d\alpha} = \left(\frac{1}{1-\alpha} - \frac{1}{\alpha} \right) \frac{1}{2.303} = - \left(\frac{1}{\alpha - \alpha^2} \right) \frac{1}{2.303} \quad (5)$$

und hieraus

$$\frac{d\alpha}{dpH} = -(\alpha - \alpha^2) 2.303 \quad (6)$$

ihr Wert lässt sich in Kenntnis von K_a auf Grund der Gleichung (2) für jeden pH-Wert berechnen, d.h. also, dass auch $d\alpha/dpH$ für jeden pH-Wert berechnet werden kann. K_a ist gleichfalls ein auf Grund der pH-Abhängigkeit der katalytischen Stufe berechenbarer Wert (3). Da α in erster Annäherung als proportional mit der Stufenhöhe betrachtet werden kann, so ist — wenn man voraussetzt, dass alles in der Umgebung der Elektrode befindliche Tetraäthylammoniumbromid Proton abgibt — die Richtungstangente der Funktion katalytischer Strom-Tetraäthylammoniumbromid-Konzentration identisch mit $d\alpha/dpH$. Der Wert dieses Differentialquotienten kann graphisch bestimmt werden. Die Tangente lässt sich nur zum Anfangsabschnitt der Kurve konstruieren, da die Ableitung die Wirkung des Tetraäthylammoniumbromids als Elektrolyt unberücksichtigt lässt; es kann also der zu 0 Tetraäthylammoniumbromid gehörende extrapolierte $d\alpha/dpH$ -Wert mit dem aus Gleichung (6) berechneten Wert verglichen werden. Um die Berechnung zu erleichtern, wird die Gleichung (6) für zwei pH-Werte aufgeschrieben, der Quotient der beiden Werte gebildet, d.h.

$$\frac{\left(\frac{d\alpha}{dpH} \right)_{pH_1}}{\left(\frac{d\alpha}{dpH} \right)_{pH_2}} = \frac{\alpha(pH_1) - \alpha(pH_1)^2}{\alpha(pH_2) - \alpha(pH_2)^2} \quad (7)$$

Da bei der vorherigen Ableitung mit dem pH-Wert gerechnet und angenommen wurde, dass jedes an der Elektrodenoberfläche befindliche Tetraäthylammonium-Ion ein freies Proton abgibt, muss die Zunahme des katalytischen Stromes auf Grund der logarithmischen Funktion berechnet werden. Da die Kurve mit logarithmischer Abszisse in Richtung zu sehr niedrigen Konzentrationen allmählich verflacht, wurden zu den Berechnungen die bei der 2. und 3. niedrigsten Tetraäthylammoniumbromid-Konzentration gemessenen Werte des katalytischen Stromes verwendet.

Nachfolgend werden die beim Methylenblau und Nikotinsäureamid gemessenen Werte zusammengefasst. Tabelle III zeigt die zu drei pH-Werte gehörenden Daten des Methylenblaus, und in Tabelle IV sind die zu zwei pH-Werten gehörenden Daten des Nikotinsäureamids zusammengefasst. Als Dissoziationskonstanten wurden bei beiden Verbindungen die Literaturwerte benutzt^{2,3}.

TABELLE III

ZUSAMMENFASSUNG DER GEFUNDENEN UND BERECHNETEN WERTE DES METHYLENBLAUS

pH	C_{H^+}	α	$(\alpha - \alpha^2)$	$\left(\frac{d\alpha}{dpH} \right)_{gem.}$
6.40	$3.99 \cdot 10^{-7}$	0.28	0.21	79.7
6.85	$1.41 \cdot 10^{-7}$	0.12	0.11	65.7
7.62	$2.40 \cdot 10^{-8}$	0.02	0.02	6.18

TABELLE IV

ZUSAMMENFASSUNG DER GEFUNDENEN UND BERECHNETEN WERTE DES NIKOTINSÄUREAMIDS

pH	C_{H^+}	α	$(\alpha - \alpha^2)$	$\left(\frac{d\alpha}{dpH}\right)_{gem.}$
5.25	$5.62 \cdot 10^{-6}$	0.101	0.09	19.5
5.40	$3.98 \cdot 10^{-6}$	0.073	0.07	12.7

Die Tabellen V und VI zeigen die Werte der auf Grund der Tabellen III und IV mit Hilfe der Gleichung (7) berechneten und gefundenen Quotienten.

TABELLE V

VERGLEICH DER AUF GRUND DER GLEICHUNG (7) BERECHNETEN UND DER GEFUNDENEN WERTE IM FALLE DES METHYLENBLAU

Die beiden Vergleichs-pH-Werte	Quotient der gemessenen Werte	Quotient der berechneten Werte
6.4–6.85	1.2	1.8
6.85–7.62	10.5	5.2
6.40–7.62	12.9	10

TABELLE VI

VERGLEICH DER AUF GRUND DER GLEICHUNG (7) BERECHNETEN UND DER GEFUNDENEN WERTE IM FALLE DES NIKOTINSÄUREAMID

Die beiden Vergleichs-pH-Werte	Quotient der gemessenen Werte	Quotient der berechneten Werte
5.25–5.40	1.5	1.3

Aus den Daten geht hervor, dass die annähernde Berechnung für die Richtigkeit der Hypothese spricht. Die Ursache der Streuung kann im Falle des Methylenblaus auch darin liegen, dass dieses bei Veränderungen des pH-Wertes Polymerisations-Gleichgewichtserscheinungen zeigt, was auch eine dauernde Veränderung der Dissoziationskonstante nach sich zieht.

ZUSAMMENFASSUNG

Verfasser untersuchten die Wirkung des Tetraäthylammoniumbromids auf den katalytischen polarographischen Strom. Bei der theoretischen Erklärung der als experimentelles Ergebnis erhaltenen Funktion wurde mit Hilfe quantitativer Auswertung nachgewiesen, dass das Tetraäthylammoniumbromid die Protonenkonzentration an der Elektrodenoberfläche erhöht und somit bei niedrigen Salzkonzentrationen eine Erhöhung der katalytischen Stufe verursacht. Bei Erhöhung der Salzkonzentration wird diese Zunahme überkompensiert, dies äussert sich über einer bestimmten Salzkonzentration in der Abnahme der Funktion.

SUMMARY

The effect of tetraethyl ammonium bromide on the catalytic polarographic current was studied. It was found to increase proton concentration on the electrode surfaces, thus increasing the catalytic wave at low salt concentrations. At higher concentrations an overcompensation of the increase occurs.

LITERATUR

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CHRONOPOTENTIOMETRIC STUDY OF OXYGEN REDUCTION AT
A PLATINUM WIRE CATHODE

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The only previously published chronopotentiometric study of the reduction of dissolved oxygen in aqueous media is that of BERZINS AND DELAHAY¹, who employed a mercury cathode, and, as expected from the known polarographic characteristics of oxygen, found stepwise reduction to hydrogen peroxide and then to water. In the present investigation the reduction of oxygen at a platinum wire cathode has been studied, and the observations prove conclusively that, in contradistinction to reduction at a mercury cathode, reduction at a platinum cathode proceeds directly to water (or hydroxyl ion) in both acid and alkaline media.

This study has not established the detailed mechanism of oxygen reduction at a platinum cathode; it has only established the net reaction. It does, however, provide cogent evidence that the platinum-platinum oxide couple is intimately involved in whatever the detailed mechanism may be. As the author pointed out a few years ago², platinum is by no means as "noble" as traditionally assumed, and there is good reason to believe that the potential of a platinum electrode always is primarily governed by a platinum-platinum ion couple. During recent years the efforts of several investigators³⁻¹⁵ have provided evidence which points very clearly to the participation of platinum-platinum ion couples in all reactions at a platinum electrode. This study adds to this evidence.

EXPERIMENTAL

The platinum wire electrode was the same one used in previous investigations^{14,15}; it was 1.59 cm long, with a radius of 0.0252 cm, and an area (exclusive of the end) of 0.251 cm². It was sealed into the end of a soft glass tube and positioned vertically in the solution. The electrolysis cell (shown in Fig. 2, *J. Electroanal. Chem.*, 1 (1960) 380) had a capacity of 100 ml. All quantitative measurements were made with the cell in a water thermostat at 25.00°.

The same electrical circuit used in preceding studies^{14,15} was employed, and the constant electrolysis current was known to $\pm 0.1\%$. The transition time, τ , was measured with a Dumont 403 cathode ray oscilloscope as described in a previous paper¹⁴. Only for qualitative purposes, complete chronopotentiograms were recorded with a strip-chart potentiometer recorder whose full-scale response time was 1.8 sec. The chronopotentiograms reproduced herein are the actual recorded curves, not tracings.

Highest purity commercial tank oxygen was used to saturate the solutions at the prevailing atmospheric pressure (760 to 768 mm). The supporting electrolytes used

were 1 *M* sulfuric acid, 1 *M* perchloric acid and 1 *M* sodium hydroxide. They were prepared from the purest commercial materials ("Analytical Reagent" grade) in distilled water whose specific conductance was $2 \cdot 10^{-6}$ ohm $^{-1}$ cm $^{-1}$.

Between trials the solution was kept stirred by bubbling the oxygen through it, but before the transition time was measured the oxygen stream was diverted above the solution and a period of at least 1 min was allowed for the solution to become quiescent. From data presented by SEIDELL¹⁶, the concentration of dissolved oxygen under the conditions of these experiments was $1.05 \cdot 10^{-6}$ moles/cm 3 in 1 *M* sulfuric acid and $0.845 \cdot 10^{-6}$ moles/cm 3 in 1 *M* sodium hydroxide, as compared to $1.28 \cdot 10^{-6}$ moles/cm 3 in pure water. The writer was unable to find a value in the literature for the solubility of oxygen in 1 *M* perchloric acid, but from observed transition times in this study it appears to be considerably larger than in 1 *M* sulfuric acid.

RESULTS AND DISCUSSION

Characteristics of the oxygen chronopotentiogram

Very early in this study it was discovered that the characteristics of the cathodic chronopotentiogram of oxygen reduction in both 1 *M* sulfuric and 1 *M* perchloric acids are critically dependent on the previous redox history of the electrode. In particular the presence of some platinum oxide(s) on the electrode surface appears to be essential to the reduction of oxygen. With a platinum cathode that has stood in oxygen-saturated 1 *M* sulfuric acid (or perchloric acid) for a long time (a day or more) there is scarcely any indication of oxygen reduction; the potential drops immediately to the value at which hydrogen ion is reduced.

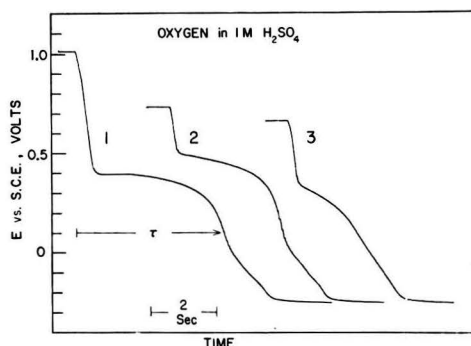


Fig. 1. Chronopotentiograms of oxygen reduction in 1 *M* sulfuric acid saturated with pure oxygen at 1 atm at 25°. In all cases the constant current was 252 μ A. (1) Platinum wire electrode pre-oxidized by anodization for 20 sec. (2) Repeated immediately without re-oxidizing the electrode. (3) Repeated after 90 min. These are the original recorded curves, not tracings.

After the electrode has been anodized briefly (*e.g.*, 20 sec with a current density of 500 μ A/cm 2 is ample), which films it with platinum oxide(s), reduction of oxygen proceeds readily at it to produce a very well-defined cathodic chronopotentiogram as shown by curve 1 in Fig. 1. Subsequent cathodic chronopotentiograms (without re-oxidation of the electrode) remain well-defined, as shown by curve 2 in Fig. 1, provided that they are recorded soon after the first one. As the elapsed time between the first

cathodic chronopotentiogram (freshly oxidized electrode) and subsequent ones increases the wave deteriorates and the transition time decreases (curve 3 in Fig. 1). These observations pertain to an acid solution kept saturated with oxygen at 1 atm and stirred by the oxygen gas stream between trials.

In the first cathodic trial with a freshly oxidized electrode (curve 1 in Fig. 1) part of the constant current results from the reduction of the platinum oxide(s). The first trial reduces most (but not quite all) of the platinum oxide(s), so that in subsequent trials the current efficiency for oxygen reduction closely approximates 100%, and the transition time is diffusion-controlled, provided the subsequent trials are made soon after the first. When a relatively long time elapses after the first trial the transition time in subsequent trials (*e.g.*, curve 3 in Fig. 1) is not controlled by the rate of oxygen diffusion to the electrode surface but rather by the rate of the slowest step in the overall electrode process itself.

Note that when the electrode is freshly oxidized (curve 1 in Fig. 1) the potential at which the reduction wave of oxygen begins (+0.40 V *vs.* S.C.E.) is significantly more negative than in an immediately subsequent trial (+0.50 V for curve 2). Although the presence of some platinum oxide(s) appears to be necessary for rapid reduction of oxygen (and probably most other substances), when the electrode is fully filmed with PtO + PtO₂ the overpotential for oxygen reduction is greater than when the electrode carries only an incomplete film. DAVIS¹³ drew essentially this same conclusion from a study by a different technique of the reduction of other substances. That the oxide film on the freshly oxidized electrode contains both PtO and PtO₂ (molar ratio PtO/PtO₂ *ca.* 6/1) was demonstrated conclusively by ANSON AND LINGANE⁹.

The potential at which the reduction wave of oxygen begins coincides very closely with the potential at which the reduction of the PtO + PtO₂ film begins, and this potential (+0.5 V *vs.* S.C.E. or +0.74 V *vs.* N.H.E.) is about 0.5 V more negative than the reversible potential of the O₂/H₂O couple in acid medium. The potential of oxygen reduction happens to coincide almost exactly with the indirectly evaluated standard potential of the O₂/H₂O₂ couple (+0.682 V *vs.* N.H.E. or +0.44 V *vs.* S.C.E.) although, as demonstrated below, the net reaction is reduction of oxygen to water rather than hydrogen peroxide.

You will have noticed in Fig. 1 that the main reduction wave of oxygen is followed by a small wave beginning at 0 V *vs.* S.C.E. A wave of exactly similar characteristics, at exactly the same potential, is always observed in the reduction of an oxidized platinum electrode in oxygen-free 1 M sulfuric acid⁹. Therefore this post-wave is believed to result from the reduction of one or another of the platinum oxides. In the present experiments it is magnified along the time axis by the fact that most of the current is associated with reduction of oxygen; *i.e.*, this is the normal enhancement of the transition time by the prior and concomitant electroreduction of another substance. Note that this post-wave does not disappear after the first trial, but is still present undiminished in curve 2 of Fig. 1. The reason is that, even though all the the platinum oxide(s) may be reduced during the first trial, as soon as the electrolysis is interrupted the reduced platinum electrode reacts rapidly with the dissolved oxygen to again produce some platinum oxide on its surface. Although the quantity of platinum oxide(s) thus produced by direct reaction with oxygen is small compared to the quantity present when the electrode is "fully oxidized" by anodization it is

a cardinal factor in the mechanism of oxygen reduction; without it the electrode loses its ability to support the electroreduction of oxygen at a rapid rate and the overall process ceases to be diffusion-controlled.

After being freshly anodized (curve 1 in Fig. 1) the "open circuit" potential of the platinum electrode invariably is close to $+1.00$ V vs. S.C.E. (or $+1.24$ V vs. N.H.E.), which is very close to the standard potential ($+1.23$ V vs. N.H.E.) of the O_2/H_2O couple. After the first cathodic trial the potential of the electrode characteristically returns to $+0.74$ V vs. S.C.E. ($+0.98$ V vs. N.H.E.) which is exactly the standard potential of the PtO/Pt couple in acid medium. It keeps returning to this value on successive trials, provided these are made within about 30 min of the first trial. On long standing after the first trial the "open circuit" potential decays to the neighborhood of $+0.65$ V (curve 3 in Fig. 1) but does not decrease much further. These "open circuit" potentials are perfectly reproducible, and certainly their close agreement with the standard potentials of the O_2/H_2O and PtO/Pt couples is not an accidental circumstance. One cannot evade the conclusion that, after the first cathodic trial, the "open circuit" potential is governed by the PtO/Pt couple.

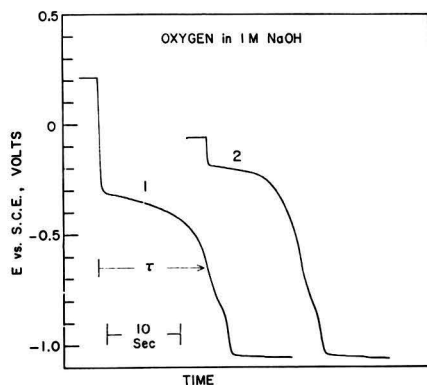


Fig. 2. Chronopotentiograms of oxygen reduction in 1 *M* sodium hydroxide saturated with oxygen at 1 atm at 25°. The constant current was 116 μ A in both cases. (1) Platinum wire electrode pre-oxidized by anodization for 20 sec. (2) Repeated without re-oxidizing the electrode. These are the original recorded curves, not tracings.

Typical chronopotentiograms for the reduction of oxygen in strongly alkaline medium (1 *M* sodium hydroxide) are shown in Fig. 2. Just as in acid media the potential at which the reduction of oxygen begins with a freshly anodized electrode (curve 1) is about 100 mV more negative than in subsequent trials. In contradistinction to the behavior in acid medium, the wave in alkaline medium does not deteriorate with elapsed time after the first trial. Hence in the practical chronopotentiometric determination of oxygen the use of an alkaline supporting electrolyte would be preferable to an acid medium.

Just as in acid medium the main reduction wave in alkaline medium is followed by a small, reproducible wave (at -0.8 V) whose position on the voltage axis coincides with an exactly similar small post-wave observed in the reduction of the PtO + PtO₂ film in alkaline medium⁹.

In 1 *M* sodium hydroxide the potential at which reduction of oxygen begins (-0.32 V with a freshly anodized electrode and -0.20 V in subsequent trials) is 0.70 V more negative (reducing) than in 1 *M* sulfuric acid. This difference is very nearly what one would expect (0.83 V) between $\text{pH} = 0$ and $\text{pH} = 14$ for a reversible reduction when the number of hydrogen ions equals the number of electrons. However, because the reduction of oxygen does not proceed with thermodynamic reversibility, the concordance of these values merely shows that the overpotential is approximately the same in acid and alkaline media. It is significant, however, that the "open circuit" potentials ($+0.22$ V vs. S.C.E. with a freshly anodized electrode and -0.06 V in subsequent trials) are very close to the respective standard potentials at $\text{pH} = 14$ of the $\text{O}_2/\text{H}_2\text{O}$ couple ($+0.16$ V vs. S.C.E.) and the PtO/Pt couple (-0.09 V vs. S.C.E.). Therefore, just as in acid media, the "open circuit" potential in alkaline medium (after the first trial) is governed by the PtO/Pt couple.

The deterioration of the oxygen reduction wave in acid medium with elapsed time after the first cathodic trial with a freshly anodized platinum electrode, and the consequent decay of the transition time, has, *a priori*, two interpretations: (a) a change from a 4-electron reduction of oxygen to water to a 2-electron reduction to hydrogen peroxide, or (b) continuing 4-electron reduction to water but a shift of control of the transition time from the rate of diffusion of oxygen to the electrode surface to the rate of the slowest step in the kinetic mechanism of the net reduction reaction. The observations summarized below accord well with what one would expect from alternative (b).

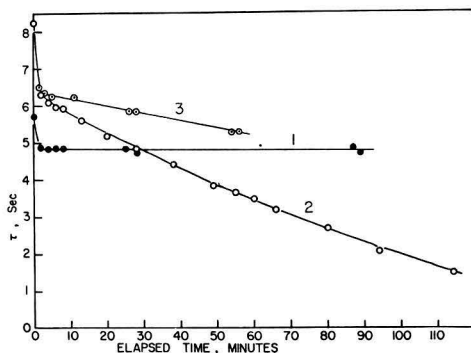


Fig. 3. Effect of elapsed time on the transition time for oxygen reduction. In all cases the platinum wire electrode had initially been pre-oxidized by anodization for 20 sec with $185 \mu\text{A}$, and the cathodic transition times were measured with a current of $185 \mu\text{A}$. The solutions were saturated with oxygen at 1 atm, and were stirred by the oxygen stream between successive trials. The successive trials were made without re-oxidizing the electrode. (1) In 1 *M* sodium hydroxide. (2) In 1 *M* sulfuric acid. After 18 h τ was smaller than 0.5 sec. (3) In 1 *M* sulfuric acid partially saturated with platinum oxide(s).

Fig. 3 shows the rate of decay of the transition time with elapsed time observed in typical experiments. In all cases the platinum wire electrode was initially oxidized by anodization for 20 sec at $185 \mu\text{A}$. The cathodic transition time was then measured as a function of elapsed time. Elapsed time was measured from the time the first

trial was made with the freshly oxidized electrode. Between successive trials the solution was kept stirred by bubbling the oxygen through it. Electrolysis was stopped, and the transition time measured at $+0.10$ V vs. S.C.E. in 1 M sulfuric acid and at -0.65 V in 1 M sodium hydroxide; *i.e.*, the potential was not allowed to decrease to the value at which hydrogen ion is reduced.

Note the constancy of the transition time in 1 M sodium hydroxide (curve 1 in Fig. 3), but its steady decrease in 1 M sulfuric acid. If the decay of τ were caused by a shift from a 4-electron reduction of oxygen to water to a 2-electron reduction to hydrogen peroxide then the decay should have stopped, and τ should have become constant, when it reached a value of $1/4$ the initial value. In curve 2 of Fig. 3 the point at 113 min happens to correspond closely to this condition. However, the decrease of τ did not cease at this point, and after 18 h τ had decayed to less than 0.5 sec.

The fact that deterioration of the oxygen wave, and consequent decay of τ , occurs only in acid medium, but not at all in alkaline medium, strongly indicates that the decay results from the gradual dissolution of the small quantity of platinum oxide(s) on the electrode surface whose presence is essential for rapid reduction of oxygen. In alkaline medium the platinum oxides are so insoluble that such dissolution does not occur. Furthermore both the rate and extent of the direct reaction of the platinum surface with dissolved oxygen are greater in alkaline than in acid media (*vide infra*); in alkaline medium if the critical oxide film is reduced by cathodization it reforms very quickly after electrolysis is interrupted.

It was discovered that the observed percentage rate of decay of τ in acid medium depends on the magnitude of the current, and becomes less the smaller the current. For example, in an experiment identical with that of curve 2 of Fig. 3, except that the current was 116 instead of 185 μ A (initial τ 21 sec instead of 6.3 sec) the percentage rate of decay was only one-third that of curve 2. This effect is consonant with the postulate that τ decays because of a shift from diffusion-control to kinetic-control. With the smaller current (longer available reaction time), the inhibiting effect of the slow step in the reaction mechanism would be expected to become relatively less important.

Curve 3 in Fig. 3 was measured in 1 M sulfuric acid like curve 2, except that the solution had previously been partially saturated with platinum oxide(s). This was done by placing a large (24 cm²) platinum electrode in the solution and polarizing it anodically for 68 min with a current of 185 μ A. Following this treatment the rate of decay of τ is much smaller (curve 3) than when the solution is originally devoid of platinum ions (curve 2). It is understandable that the rate of dissolution of platinum oxide(s) from the platinum wire electrode should be smaller if the solution originally contains platinum ions.

Apparently the solubilities of none of the platinum oxides have ever been measured directly. As a very rough estimate LATIMER¹⁷ has guessed that the solubility product of $\text{Pt}(\text{OH})_2$ is about 10^{-35} . If so, the concentration of Pt^{2+} in a solution 1 M in hydrogen ion saturated with $\text{Pt}(\text{OH})_2$ would be 10^{-7} M. Although the solubility may be somewhat increased by complexation with HSO_4^- ion it is improbable that the total concentration of dissolved platinum in the experiment of curve 3 of Fig. 3 could have been larger than about 10^{-5} M. This concentration is so small compared to the concentration of oxygen ($1.05 \cdot 10^{-3}$ M) that reduction of platinum ions could not have significantly increased the transition time.

The rate of decay of τ is not effected by the number of measurements made during a given total elapsed time interval; under a given set of conditions it depends only on elapsed time. In a specific experiment to test this point eleven successive trials were made in an elapsed time of only 16 min. The total decay of τ was the same as when only three trials were made during the same elapsed time. This is cogent evidence against the possibility that the decay of τ might be caused by the gradual accumulation of some impurity, since the amount of impurity deposited on the electrode surely would increase with the number of successive trials.

Further evidence that the deterioration of the oxygen wave is not caused by the accumulation of an impurity on the electrode is the fact that the rate of decay of τ was found to be exactly the same when the solution was prepared in specially purified water (re-distilled twice from a quartz vessel) as when ordinary distilled water was used.

With both 1 *M* sulfuric and perchloric acids it was observed that after the transition time had decayed considerably it could be partially restored by cathodizing the platinum electrode to the potential (-0.24 V *vs.* S.C.E.) at which hydrogen ion is reduced. Alternatively, if successive trials are made by recording the entire chronopotentiogram to the potential of hydrogen ion reduction the rate of decay of τ is much smaller than when the electrolysis is interrupted in each trial at the "transition potential" ($+0.10$ V *vs.* S.C.E. in 1 *M* sulfuric acid). During such cathodization the platinum oxide(s) on the electrode is reduced to the metal, and in addition there must be some reduction to the metal of the small concentration of platinum ions in the solution. This freshly deposited platinum doubtless is more reactive than the original platinum surface, and its oxidation by the dissolved oxygen probably produces more platinum oxide(s) than was present immediately prior to cathodization, so that the electrode is partially rejuvenated in respect to its "catalytic activity" for oxygen reduction.

When the electrode is in the oxidized condition, produced by polarizing it anodically, it may be left for hours in 1 *M* sulfuric acid and when the cathodic chronopotentiometric trials are finally begun the results are identical with those obtained when the trials are made immediately after anodization.

Neither the time of the pre-anodization used to "activate" the electrode nor the current are critical. Anodic polarization only to the potential at which the film of PtO + PtO₂ is formed ($+1.25$ V *vs.* S.C.E.) is just as effective as prolonged polarization to the potential of oxygen evolution.

Reduction product of oxygen

That oxygen is reduced all the way to water (or hydroxyl ion) at a platinum cathode, rather than to hydrogen peroxide, was established by comparing the observed transition time with the theoretical values for a 4- and 2-electron reduction.

In previous communications^{14,15} it was demonstrated that when the transition time τ is governed by cylindrical diffusion to a wire electrode

$$\frac{i\tau^{1/2}}{C} = \frac{\pi^{1/2} n F A D^{1/2}}{2} \left[1 - \frac{\pi^{1/2} D^{1/2} \tau^{1/2}}{4r} + \frac{D\tau}{4r^2} - \frac{3\pi^{1/2} D^{3/2} \tau^{3/2}}{32r^3} + \frac{21D^2\tau^2}{160r^4} - \dots \right] \quad (1)$$

where i is the constant current (A), C is the concentration of the electroactive substance (moles/cm³), n is the number of electrons per molar unit of reaction, F is the faraday constant (96,493 coulombs), A is the area of the wire electrode (cm²), D is the diffusion coefficient (cm²/sec), π is 3.1416, and r is the radius of the wire electrode (cm). That this relation has general validity has been established conclusively from studies of the oxidation of oxalic acid, oxidation of hydroquinone, reduction of quinone, reduction of ferric iron, and reduction of hydrogen ion^{14,15}. When the quantity $i\tau^{1/2}/C$ is measured over a range of current densities (to produce a range of transition times) a plot of the values against τ extrapolates at $\tau = 0$ to $\pi^{1/2}nFAD^{1/2}/2$ which is the familiar SAND relation for the case of restricted linear diffusion to a plane electrode; *i.e.*, the denominator in eqn. 1 approaches unity either when τ approaches 0 or when r becomes infinitely large. However, under the conditions of the present experiments the complete eqn. 1 is necessary to interpret the observed transition times as a function of n , and thus to establish the reduction product of oxygen.

It should be emphasized that eqn. 1 will be valid whenever the process which controls τ follows a *first order* rate law. In the usual case this first order process will be diffusion, but it might also be a first order reaction at the electrode if the rate constant of such a reaction were sufficiently small. Consequently to evaluate n it is not sufficient merely to demonstrate that the shape of the $i\tau^{1/2}/C$ vs. τ curve follows the shape of eqn. 1, but it is necessary to prove that the actual values of $i\tau^{1/2}/C$ observed over a range of current densities agree quantitatively with those calculated *via* eqn. 1 from independent measurements of the diffusion coefficient D .

From the observations summarized above it is evident that the transition time will be governed by the rate of diffusion of oxygen to the electrode (and hence eqn. 1 will be valid) only if the electrode has on its surface enough platinum oxide(s) so that the slowest step of the reaction sequence at the electrode surface proceeds faster than the rate of diffusion of oxygen from the body of the solution. Therefore, the transition time measurements in 1 *M* sulfuric acid cited below were made as follows. Before each measurement at the different current densities the electrode was anodized for 20 sec with a current of 185 μ A. Successive measurements of the cathodic transition time at the particular current density were then made in rapid succession, discarding the first trial. The solution was stirred briefly (15 to 30 sec) by the oxygen stream between trials. The first trial in each case was discarded because it includes a contribution from the reduction of the platinum oxide(s) formed by the pre-anodization. The quoted values of τ are the average of two or three subsequent trials made within 5 min of the first trial.

The measurements in 1 *M* sodium hydroxide were made by pre-anodizing the electrode only at the start of the series of trials. It was not necessary to pre-anodize it between each trial at the different current densities (see Fig. 3).

The results of the transition time measurements made in this way over a wide range of current densities are summarized in Tables I and II. The transition time was measured from the instant the circuit was closed to the moment the "transition potential" was reached. The arbitrarily selected transition potentials were +0.10 V vs. S.C.E. in 1 *M* sulfuric acid (see Fig. 1) and -0.65 V vs. S.C.E. in 1 *M* sodium hydroxide (see Fig. 2).

In 1 *M* sodium hydroxide a small part of the observed current results from the reduction of part of the platinum oxide(s) on the electrode surface, which, after each

TABLE I

OXYGEN REDUCTION IN 1 M SODIUM HYDROXIDE

1 M NaOH sat'd. with oxygen at 1 atm at 25.00°; $i_{corr.} = i_{obs.} - 63/\tau$; $C = 8.45 \cdot 10^{-7}$ moles/cm³.

$i_{obs.} (\mu A)$	τ (sec)	$i_{corr.} (\mu A)$	$i\tau^{1/2}/C (A \cdot sec^{1/2} \cdot cm^3/mole)$	
			Observed	Corrected
552.0	0.59 ± 0.01	445	502	403
395.1	1.12 ± 0.003	339	495	425
345.9	1.38 ± 0.01	300	482	418
307.6	1.69 ± 0.01	271	474	417
251.9	2.58 ± 0.02	228	478	433
223.6	3.26 ± 0.01	205	478	438
185.0	4.77 ± 0.05	172	478	445
163.3	6.11 ± 0.02	153	478	448
146.2	7.78 ± 0.03	138	483	456
136.2	9.04 ± 0.02	129	485	459
126.3	10.65 ± 0.10	120	488	463
111.4	14.13 ± 0.01	107	496	476

TABLE II

OXYGEN REDUCTION IN 1 M SULFURIC ACID

1 M H₂SO₄ saturated with oxygen at 1 atm at 25.00°; $C = 1.05 \cdot 10^{-6}$ moles/cm³; before each trial the electrode was freshly anodized as described in the text.

$i_{obs.} (\mu A)$	τ (sec)	$i\tau^{1/2}/C$ ($A \cdot sec^{1/2} \cdot cm^3/mole$)
625.8	0.54 ± 0.02	438
551.5	0.69 ± 0.01	436
394.8	1.32 ± 0.00	432
345.6	1.78 ± 0.02	439
307.4	2.20 ± 0.00	434
251.7	3.38 ± 0.04	442
223.4	4.35 ± 0.05	444
203.8	5.34 ± 0.03	448
184.9	6.70 ± 0.02	456
163.2	8.98 ± 0.05	466
146.0	11.58 ± 0.03	473
136.1	13.76 ± 0.06	482
126.2	16.69 ± 0.06	492

cathodic trial, is rapidly produced by the direct reaction of the platinum with dissolved oxygen. In strongly alkaline medium this direct reaction occurs very rapidly as soon as electrolysis is interrupted, but the amount of platinum oxide(s) thus formed is far smaller than a complete film of PtO + PtO₂. Consequently a "blank correction" for this effect is necessary, particularly at the shorter transition times.

This "blank correction" was evaluated as follows. Oxygen was completely displaced from the cell and solution with high purity nitrogen and the electrode was cathodized briefly to the potential of hydrogen evolution to insure that any oxide originally on it was completely reduced. The electrode was removed from the cell and placed in oxygen-saturated 1 M sodium hydroxide for a measured time. The electrode was then replaced in the cell and, after passing nitrogen through the solution

for 15 min to remove traces of oxygen introduced with the electrode, the "blank" transition time to -0.65 V was measured with a current of $15.1 \mu\text{A}$. It was found that the reduced electrode was oxidized very quickly on exposure to oxygen; after only 1 min exposure the blank transition time was the same as after 20 min exposure. The average blank transition time from several trials was 4.2 ± 0.2 sec with a current of $15.1 \mu\text{A}$, corresponding to a "blank" quantity of electricity, Q , of $63 \pm 3 \mu\text{coulombs}$. This is about one-fourth the value for a complete film of $\text{PtO} + \text{PtO}_2$.

The observed current during an actual chronopotentiometric reduction of oxygen was corrected for this blank by the empirical relation $i_{\text{corr.}} = i_{\text{obs.}} - (63/\tau)$, where τ is the actual observed transition time. The justification of this method of applying the blank correction has been discussed in detail in previous papers^{14,15}. In Table I values of the "transition time constant" $i\tau^{1/2}/C$ based on both the observed and corrected current are listed.

An attempt was made to evaluate the blank correction in 1 *M* sulfuric acid by the same technique used in alkaline media. However, the oxide film produced on the electrode by exposure to oxygen dissolved off so rapidly when the electrode was replaced in oxygen-free 1 *M* sulfuric acid that the blank transition time could not be accurately evaluated. Therefore only observed values of $i\tau^{1/2}/C$ are listed in Table II. It should be possible to evaluate the blank by employing oxygen-free 1 *M* sulfuric acid that is also saturated with the platinum oxides, but this was not tried. From indirect evidence the blank in acid medium is known to be much smaller than in alkaline medium (perhaps 15 to 20 $\mu\text{coulombs}$); it is large enough to significantly increase the smaller observed transition times (below about 2 sec) but yet is small enough not to seriously effect the transition time when the latter is greater than about 2 sec.

To establish the reduction product of oxygen from the data in Tables I and II (*i.e.*, to evaluate n in eqn. 1) it is necessary to know the diffusion coefficient, D , of oxygen. The only D value extant in the literature is that ($2.6 \cdot 10^{-5}$ cm^2/sec) reported by KOLTHOFF AND MILLER¹⁸, from polarographic measurements with the dropping mercury electrode, and this value pertains to 0.1 *M* potassium nitrate rather than to the solutions used in the present study. It should also be noted that KOLTHOFF AND MILLER adduced this value by using the original form of the ILKOVIC equation (since no other relation was available at the time of their study). Because the original ILKOVIC equation ignores the curvature of the mercury drop values of D derived from it are considerably larger than the true values. Much more nearly correct values of D result when one employs the modified ILKOVIC equation derived by LINGANE AND LOVERIDGE¹⁹ and STREHLOW AND VON STACKELBERG^{20,21}, which takes into account the curvature of the mercury drop. Using the original data of KOLTHOFF AND MILLER¹⁸ in conjunction with the LINGANE-LOVERIDGE modification of the ILKOVIC equation leads to a D -value of $2.0 \cdot 10^{-5}$ cm^2/sec instead of $2.6 \cdot 10^{-5}$ cm^2/sec . Because there was no *a priori* assurance that this value (in 0.1 *M* potassium nitrate) would apply to the solutions used in the present study, the diffusion coefficients of oxygen in 1 *M* sulfuric acid and 1 *M* sodium hydroxide were evaluated from polarographic diffusion currents with the dropping mercury electrode.

The polarographic measurements were performed in the usual way²¹ and the solutions were saturated with oxygen at 1 atm pressure at 25°. From the observed diffusion currents (corrected for background current), and the LINGANE-LOVERIDGE

modification of the ILKOVIC equation¹⁹, the diffusion coefficient of oxygen is $2.02 \cdot 10^{-5}$ cm²/sec in 1 *M* sulfuric acid and $1.79 \cdot 10^{-5}$ cm²/sec in 1 *M* sodium hydroxide at 25°, with a probable uncertainty of about 5% in each case.

When these values are introduced into eqn. 1, together with the known values of *A* and *r* for the platinum wire electrode, the theoretical equation in 1 *M* sulfuric acid for *n* = 4 (reduction of oxygen to water) is

$$\frac{i\tau^{1/2}}{C} = \frac{384}{[1 - 0.0788\tau^{1/2} + 0.0079\tau - 0.00093\tau^{3/2} + 0.00014\tau^2 - \dots]} \quad (2)$$

Correspondingly for 1 *M* sodium hydroxide, and *n* = 4, the theoretical equation is

$$\frac{i\tau^{1/2}}{C} = \frac{364}{[1 - 0.0747\tau^{1/2} + 0.0071\tau - 0.00079\tau^{3/2} + 0.00011\tau^2 - \dots]} \quad (3)$$

For *n* = 2 (reduction to hydrogen peroxide) the numerators in equations 2 and 3 would be respectively 192 and 182 but the denominators remain unchanged.

In Fig. 4 the experimental values of $i\tau^{1/2}/C$ from Tables I and II are plotted against τ , and the curves are plots of the theoretical equations 2 and 3. The fact that the three

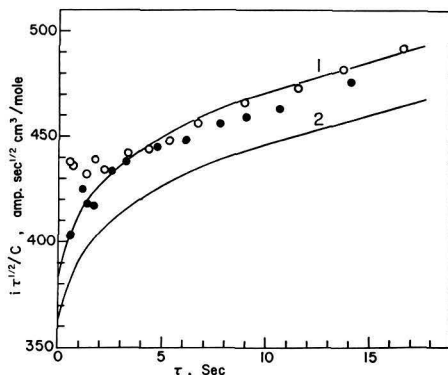


Fig. 4. Comparison of observed values of $i\tau^{1/2}/C$ with the theoretical values for *n* = 4. (1) Theoretical curve (eqn. 2) for $D = 2.02 \cdot 10^{-5}$ cm²/sec. (2) Theoretical curve (eqn. 3) for $D = 1.79 \cdot 10^{-5}$ cm²/sec. O, 1 *M* H₂SO₄; ●, 1 *M* NaOH.

or four experimental points at the shortest transition times in 1 *M* sulfuric acid lie somewhat above the theoretical curve doubtless is due to a small undetermined "blank" discussed above; a blank correction corresponding to only 20 μcoulombs would bring these four points down to the theoretical curve. The experimental points in 1 *M* sodium hydroxide are consistently somewhat above the theoretical curve for $D = 1.79 \cdot 10^{-5}$ cm²/sec. However the average discrepancy is only +4%, which is of the same order of magnitude as the probable uncertainty in the polarographically measured diffusion coefficient.

The good agreement of the experimental points in Fig. 4 with the theoretical curves

for $n = 4$ proves conclusively that in both media reduction of oxygen proceeds all the way to water rather than to hydrogen peroxide. It should be emphasized that this conclusion is not dependent on the validity of eqn. 1 (although the weight of evidence now available leaves no question of its validity). If one had no knowledge of eq. 1, and simply performed an empirical extrapolation of the observed $i\tau^{1/2}/C$ values to $\tau = 0$ (corresponding to the SAND equation), the same conclusion would be unavoidable.

Since oxygen is reduced all the way to water it might be expected that hydrogen peroxide would produce a chronopotentiometric reduction wave at a potential equal to (or more oxidizing than) the potential of the oxygen wave. Actually, it was found that in 1 *M* sulfuric acid hydrogen peroxide does not produce a cathodic wave, at either a pre-oxidized or a pre-reduced platinum electrode. It does, however, yield a well-developed anodic wave (doubtless $\text{H}_2\text{O}_2 \rightarrow \text{O}_2$) at +0.88 V vs. S.C.E. in 1 *M* sulfuric acid. Evidently, whatever the detailed kinetic mechanism may be in the reduction of oxygen, molecular hydrogen peroxide is not a transient intermediate.

Apparently the only previous study of the reduction product of oxygen at a platinum cathode is that of LAITINEN AND KOLTHOFF²², who were led to the erroneous conclusion that hydrogen peroxide is the reduction product. These authors studied the current-potential curve for the reduction of oxygen from air-saturated solutions with a stationary platinum wire cathode. The platinum cathode was not subjected to an oxidizing pre-treatment (since the importance of this was not known at the time) and the current-potential curves were measured manually with several minutes waiting at each point for a steady state current. By the time the limiting current was reached the electrode had been subjected to continuous cathodization for a considerable time. In view of the decay of activity toward oxygen reduction observed in the present study, it is well nigh certain that under the conditions of the experiments of LAITINEN AND KOLTHOFF the platinum cathode was not in a condition of maximum efficiency. Consequently the limiting current they observed must have been kinetically controlled and smaller than it would have been if the electrode had been freshly activated by anodization before each point of the current-potential curve was measured.

Temperature coefficient of τ in oxygen saturated solution

The only temperature dependent term on the right side of eqn. 1 is the diffusion coefficient, so that, in general, the temperature coefficient of $(i\tau^{1/2}/C)$ is determined only by the temperature coefficient of D . The temperature coefficient of τ itself depends in addition on the temperature coefficient of C . However, in the usual circumstance that the electroactive substance is non-volatile the temperature coefficient of C is so small (ca. -0.025%/degree) that it is unimportant and any variation of τ with temperature can be ascribed almost entirely to the temperature coefficient of D . In general for most substances the temperature coefficient of D is close to +2%/degree, and hence, in the usual case, the temperature coefficient of τ will also be close to +2%/degree.

The reduction of oxygen from solutions kept saturated with oxygen at a constant pressure is an interesting special case. With increasing temperature τ tends to increase because of the increase of D , but the molar concentration of dissolved oxygen decreases (at any given constant oxygen pressure), and these two effects counteract each

other. Indeed, the compensation is so nearly perfect that the net temperature coefficient of τ is very small.

In 1 *M* sulfuric acid measurements of τ at 35° averaged only 1.8% larger than at 25° under otherwise identical conditions. In 1 *M* sodium hydroxide the difference was only 1%. Since the precision of the measurement of τ itself is *ca.* $\pm 1\%$, it is evident that the temperature coefficient of τ is not greater than about $\pm 0.2\%$ /degree, and may be even smaller. These observations pertain to solutions saturated with oxygen at 1 atm, but presumably this net temperature coefficient will be independent of the partial pressure of oxygen.

Consequently in the practical chronopotentiometric determination of oxygen precise temperature control is unnecessary.

Analytical application

Obviously, chronopotentiometry with a platinum wire cathode can serve well for the determination of oxygen, provided the electrode is freshly anodized before each trial. The sensitivity and accuracy can be expected to be about the same as in the polarographic determination of oxygen with the dropping mercury electrode. However, a platinum wire cathode is more amenable than the dropping mercury electrode to automatic operation, and to situations (such as oxygen determination in sea-water) where the measuring element must be far removed from the observer.

The observations of this study ought to be useful in guiding the development of other electrometric methods of oxygen determination with a platinum electrode.

ACKNOWLEDGEMENT

Appreciation is expressed to the Standard Oil Foundation, Inc., for partial financial support of this investigation.

SUMMARY

This study provides conclusive proof that in both acid and basic aqueous media oxygen is reduced at a platinum cathode all the way to water rather than to hydrogen peroxide.

It was discovered that rapid, diffusion-controlled reduction of oxygen occurs only when there is some platinum oxide on the platinum cathode. It is not necessary that the electrode be fully covered by a platinum oxide ($\text{PtO} + \text{PtO}_2$) film; an amount of platinum oxide corresponding to about 80 $\mu\text{coulombs/cm}^2$ (*i.e.*, about one-tenth the amount on a fully oxidized electrode) is enough to maintain diffusion control. When the quantity of platinum oxide is much smaller than this the overall reaction becomes kinetically-controlled, but the net reaction is still a 4-electron reduction of oxygen. The platinum-platinum ion (or platinum oxide) couple must be intimately involved in whatever the detailed kinetic mechanism may be. Apparently the primary step (or steps) in the reduction of oxygen is direct "chemical" reaction between the oxygen and the platinum, and the platinum ion(s) or oxide(s) thus formed are rapidly reduced back to metallic platinum in subsequent electron-transfer steps to yield the observed current. Very probably the rate-controlling step is associated with the primary "chemical" reduction of the oxygen by the metallic platinum.

The characteristics of the chronopotentiograms of oxygen with a platinum wire

cathode in both acid and basic media are very well suited to the practical determination of oxygen. In such analytical applications the platinum electrode should be freshly oxidized by brief anodic polarization before each trial to insure that the transition time will be diffusion-controlled, and thus will be governed by the concentration of oxygen.

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ELECTROCHEMISTRY OF DISSOLVED GASES*

II. REDUCTION OF OXYGEN AT PLATINUM, PALLADIUM, NICKEL AND OTHER METAL ELECTRODES

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INTRODUCTION

Although the electrolytic reduction of dissolved oxygen has been extensively studied¹⁻¹², there is still considerable question concerning the actual electrode reaction and its mechanism. Much of the work has been with mercury electrodes, and the studies which have been concerned with solid electrodes are limited^{3,5-7,12}. During the course of the studies discussed in the first paper of this series¹, it was noted that solution composition and electrode conditioning frequently had significant effects on the oxygen reduction wave. Because of the desirability to have the best electrode system which is possible for the analysis of oxygen, a study of the effects on the reduction wave of electrode material, pH, supporting electrolyte and electrode preconditioning has been made. The results of this study are the basis for the present discussion.

The reduction of dissolved oxygen has been investigated at platinum, palladium, nickel, gold, silver, tantalum, tungsten, copper, zinc, cadmium and lead electrodes. The effect of supporting electrolyte, pH, and electrode preconditioning upon the reduction reaction has been studied voltammetrically. In the case of the platinum, palladium and nickel electrode systems, these variables have been studied further by chronopotentiometry.

RESULTS AND DISCUSSION

Voltammetry at a platinum electrode

The voltammetric reduction of oxygen has been studied at unconditioned, pre-oxidized and pre-reduced platinum electrodes as a function of pH and supporting electrolyte.

The results for the pre-reduced electrode as well as for the unconditioned electrode are similar to those observed by LAITINEN AND KOLTHOFF⁵, who noted that the reduction wave is independent of pH. In the presence of 0.1 *F* K₂SO₄, MgSO₄, NaClO₄, KCl, LiCl, KNO₃, KClO₃, KBrO₃, KIO₃ or KBr the half-wave potential for

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oxygen reduction is between -0.16 V and -0.20 V over the pH range from pH 2 to pH 12. (All potentials, unless otherwise stated, are with reference to a saturated calomel electrode, S.C.E.) When KI is used as a supporting electrolyte the half-wave potential is shifted to more negative potentials; for 0.001 F KI, $E_{1/2} = -0.27$ V; for 0.01 F or higher concentrations of KI, $E_{1/2} = -0.36$ V. The reason for this shift is probably due to the formation of PtI_2 from the initial oxide film on the platinum electrode. An oxygen reduction wave is not observed when KCN is present in significant quantities, 0.01 F or greater. Formation of cyanogen (or some other product) from the reaction of CN^- with O_2 probably accounts for the absence of a wave.

Platinum electrodes which have been pre-oxidized, either electrolytically or with strong oxidizing agents, give an oxygen reduction wave whose half-wave potential changes with pH; from $+0.30$ V at pH 2 to -0.32 V at pH 13 (curve A of Fig. 1).

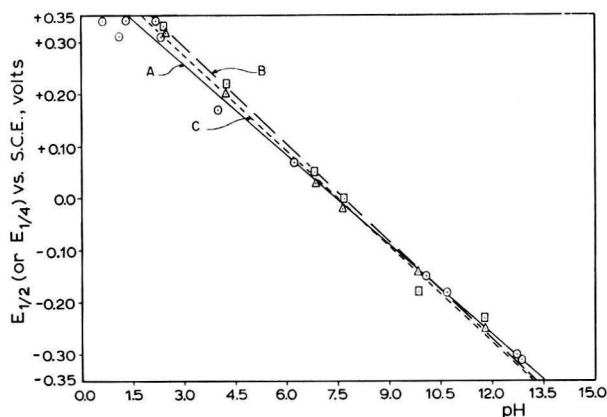


Fig. 1. Voltammetric and chronopotentiometric reduction at platinum electrodes; the half-wave (voltammetric) and quarter-wave (chronopotentiometric) potentials as a function of pH. All solutions are 0.1 F in K_2SO_4 . Curve A: \circ , voltammetric reduction of oxygen in solution, using a pre-oxidized electrode; slope is equal to -0.058 V per pH unit. Curve B: \square , chronopotentiometric reduction of oxygen in solution; current, 0.50 mA/cm²; slope is equal to -0.063 V per pH unit. Curve C: \triangle , chronopotentiometric reduction of $\text{Pt}(\text{OH})_2$. The electrode is pre-oxidized electrolytically followed by deaeration of the solution with pre-purified nitrogen; current, 0.02 mA/cm²; slope is equal to -0.061 V per pH unit.

The slope of curve A indicates that one electron per hydroxide ion is consumed in the reduction reaction. The reduction wave usually has a broad maximum which is characteristic of the pre-oxidized electrode. The wave is independent of supporting electrolyte for the electrolytes K_2SO_4 , KClO_3 , KNO_3 , NaClO_4 , KCl and KBr ; again, the presence of KCN prevents the appearance of an oxygen wave. If the voltage scan is reversed at the end of the reduction wave, then the resulting reverse wave has the characteristics of a wave obtained at a reduced electrode. Reversal of the direction of scan for a reduced electrode, on the other hand, reproduces the initial wave. The characteristics of a platinum oxide electrode are only observed for an electrode with a freshly formed oxide film. As the oxide coating ages, the reduction wave becomes less reversible, usually resulting in a change of the half-wave potential.

For solutions containing KBrO_3 and KIO_3 the oxygen wave is not observed at the pre-oxidized electrode because of the reduction of BrO_3^- or IO_3^- prior to the oxygen wave. With the reduced electrode, these two salts do not interfere with the oxygen wave. Such behavior is consistent with the observations of ANSON¹³ concerning the chronopotentiometric reduction of IO_3^- . He notes that the oxide film on platinum catalyzes the IO_3^- reduction by 0.2 to 0.6 V over its reduction at a reduced electrode. Hence, this would explain why an oxygen wave is observed in the presence of KIO_3 or KBrO_3 at a reduced electrode but not at an oxidized electrode.

The reduction of oxygen at a pre-oxidized electrode is also affected by the presence of KI. For the other electrolytes the half-wave potential becomes more negative with pH, from +0.30 V at pH 2 to -0.32 V at pH 13. However, in the case of 0.1*F* KI as the supporting electrolyte, the half-wave potential is -0.13 V at pH 2 and shifts to -0.27 V at pH 13. This would indicate that the pre-oxidized electrode reacts with the KI, particularly at low pH's.

When CaCl_2 is present as the supporting electrolyte, the pre-oxidized electrode gives a double wave. The first wave has a half-wave potential of -0.16 V and is twice as high as the second wave which has a half-wave potential of -0.34 V. At pH 2 there is only a single wave which is similar to the waves with other electrolytes. Above pH 6 the double wave is produced. The cause of this double-wave behavior is not readily explained. Adsorption phenomena may be a possible cause, although it is surprising that other electrolytes do not produce similar effects.

Voltammetry at a palladium electrode

The voltammetric reduction of oxygen at a palladium electrode is similar to that at a platinum electrode. Thus, the half-wave potential at an unconditioned electrode is -0.18 V and at a reduced electrode it is -0.21 V. Both of these forms of the electrode give reduction waves which are independent of pH. However, in the case of the reduced electrode the initial portion of the wave exhibits anodic current.

Production of a palladium oxide electrode by anodization, in a fashion analogous to the platinum oxide electrode, was usually not satisfactory. Even voltammetric oxidation at low currents gave electrodes which often were not reproducible. However, oxidation of the electrode by immersion in a $\text{Ce}(\text{NO}_3)_4\text{-HNO}_3$ solution gives an electrode which is reproducible and which has properties similar to those of the platinum oxide electrode. Again, as in the case of the platinum oxide electrode, aging of the oxide film of the palladium electrode causes it to behave less reversibly. At a freshly formed palladium oxide electrode reduction of dissolved oxygen in an unbuffered solution gives a half-wave potential of -0.18 V. Curve A of Fig. 2 shows the half-wave potential for this reduction as a function of pH. Thus it is seen that the reduction is strongly affected by the acidity of the solution. The slope of curve A indicates that one electron per hydroxide is consumed in the reduction mechanism. It is interesting to note that for both platinum and palladium electrodes oxygen reduction at pre-oxidized electrodes in solutions of approximately pH 11 occurs at essentially the same potential as it does at pre-reduced electrodes in solutions of any pH.

As with the platinum electrode, the presence of iodide ion strongly affects the reduction of oxygen at a palladium electrode. The general effect of iodide ion on oxygen reduction at platinum, palladium and nickel electrodes is discussed in detail in a later section.

Voltammetry at a nickel electrode

The reduction of dissolved oxygen has also been studied at nickel electrodes under various solution and electrode conditions. Studies at this electrode are more difficult than with the platinum and palladium electrodes, primarily because of the erratic and non-reproducible character of the electrode. In contrast to the platinum and

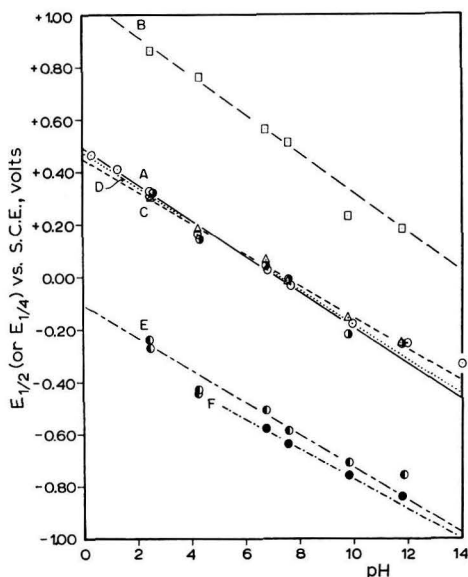


Fig. 2. Voltammetric and chronopotentiometric reduction at palladium and nickel electrodes; the half-wave (voltammetric) and quarter-wave (chronopotentiometric) potentials as a function of pH. All solutions are 0.1 *F* in K_2SO_4 . Curve A: \circ , voltammetric reduction of oxygen in solution, using a pre-oxidized palladium electrode; slope is equal to -0.068 V per pH unit. Curve B: \square , chronopotentiometric reduction of PdO_2 . The electrode is pre-oxidized electrolytically followed by deaeration of the solution with pre-purified nitrogen; current, 0.05 mA/cm²; slope is equal to -0.075 V per pH unit. Curve C: \triangle , chronopotentiometric reduction of $Pd(OH)_2$. This represents the second reduction step of the electrode; step 1 is represented by curve B; current, 0.50 mA/cm²; slope is equal to -0.060 V per pH unit. Curve D: \circ , chronopotentiometric reduction of oxygen in solution at a palladium electrode; current, 0.50 mA/cm²; slope is equal to -0.066 V per pH unit. Curve E: \circ , voltammetric reduction of oxygen in solution, using a pre-oxidized nickel electrode; slope is equal to -0.062 V per pH unit. Curve F: \circ , chronopotentiometric reduction of oxygen in solution at a nickel electrode; current, 0.50 mA/cm²; slope is equal to -0.056 V per pH unit.

palladium electrodes, the unconditioned nickel electrode does not have the characteristics of a reduced nickel electrode. In fact the unconditioned electrode gives such erratic results that it is not possible to obtain useful data with it. However, with careful attention to preconditioning operations and to the handling of the electrode consistent results are obtained. Apparently the reduction reactions for this electrode are also more complex than for either the platinum or palladium electrodes.

Although anodization produces a satisfactory oxide film on a nickel electrode, oxidation by a $Ce(NO_3)_4-HNO_3$ solution is equally satisfactory as well as being more convenient. Reduction of dissolved oxygen at a pre-oxidized nickel electrode gives a

wave which is quite drawn out with a half-wave potential of -0.50 V (0.1 F K_2SO_4 , unbuffered) (see curve A of Fig. 3). Under certain conditions this drawn-out wave actually resolves itself into two waves, especially if the electrode is subjected to repeated electrolytic reduction prior to the final pre-oxidation (see curve B of Fig. 3). The first wave of curve B is independent of pH and has a half-wave potential of

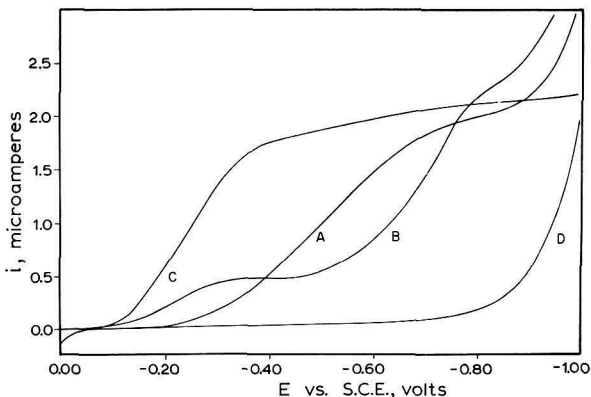


Fig. 3. Voltammetric reduction of oxygen at nickel electrodes. All solutions are 0.1 F in K_2SO_4 . The reduction curves are for an oxygen-saturated (1 atm) solution using an electrode with an area of 0.012 mm^2 . Curve A: electrode pre-oxidized for 1 min in a $Ce(NO_3)_4$ - HNO_3 solution. Curve B: electrode preconditioned by several reductions and finally pre-oxidized for 1 min in 1 F H_2SO_4 at 3 V; solution adjusted to pH 9.8 . Curve C: electrode pre-reduced for 11 min in 0.1 F K_2SO_4 at -1 V. Curve D: blank, electrode preconditioned the same as the electrode for curve B; solution adjusted to pH 9.8 .

-0.24 V. The height of this first wave relative to the height of the second wave varies with the preconditioning of the electrode, but it is usually about one-fourth the height of the second wave. The first wave, because of its independence of pH, may represent the direct reduction of oxygen under the conditions of this wave. The potential for this wave is quite similar to that of the oxygen wave at the reduced nickel electrode. The second wave of curve B is pH-dependent as is shown by curve E of Fig. 2. As with the other electrodes a freshly produced oxide coating on the electrode gives oxygen-reduction waves which are not only more reversible but which are also more reproducible.

For a nickel electrode it apparently is not possible to get a completely reduced surface in aqueous solutions. However, an electrode subjected to extensive pre-reduction gives an oxygen reduction wave whose half-wave potential is essentially independent of pH; -0.21 V at pH 2 and -0.27 V at pH 10 (see curve C of Fig. 3). Although this electrode is essentially a reduced electrode, note the increase in the reduction current at -0.6 V. This increase appears to be due to a small amount of oxide film on the electrode surface, occurring at approximately the same potential as the reduction wave for a pre-oxidized electrode (curve A of Fig. 3).

The slope for curve E of Fig. 2 indicates that one electron per hydroxide ion is involved in the reduction reaction for the pH-dependent oxygen reduction wave. Apparently the electrode reaction involves the reduction of the oxide film, $Ni(OH)_2$,

on the electrode surface. Pre-reduction removes most of the oxide film and gives a reduced surface for the reduction of oxygen. Under these conditions the reduction wave is independent of pH, with a half-wave potential and characteristics similar to the reduced platinum and palladium electrodes.

Voltammetry at other metal electrodes

A series of other metal electrodes has been studied with respect to the reduction of dissolved oxygen. When possible, these electrodes have been studied in the pre-oxidized and pre-reduced as well as the unconditional state.

The pre-reduced forms of the gold and silver electrodes give reduction waves almost identical to the waves for the pre-reduced platinum electrode. The half-wave potential for both electrodes is -0.17 V and is independent of pH. For the remainder of the metal electrodes it is not possible to maintain a reduced electrode in the presence of oxygen. In the case of Cu, Cd, Zn, Pb and W electrodes the reduction of the large amount of metal oxide obscures any contribution due to dissolved oxygen. The metal oxides for these electrodes are formed so rapidly by the dissolved oxygen that it is not possible to observe any wave for oxygen. That the dissolved oxygen is not reduced prior to the reduction of the metal oxide is interesting, particularly for the Cd, Zn and Pb electrodes. These three electrodes give oxide reduction waves which begin at -0.72 V, -1.02 V and -0.5 V, respectively. Also, all three electrodes exhibit anodic current at potentials more positive than that of oxide reduction; this anodic current would obscure an oxygen reduction wave. For the Ag and Au electrodes the oxide is reduced prior to the oxygen wave, and thus these electrodes act as reduced electrodes for the oxygen wave. Because copper oxide is reduced at approximately the same potential as the reduction of oxygen at a reduced electrode, erratic results are frequently observed with the copper electrode.

Pre-oxidation of this group of electrodes, except in the case of tantalum and tungsten, produces oxide coatings which are sufficiently soluble to prohibit useful studies of the oxygen reduction wave. At pH 2 the unconditioned tantalum electrode does not exhibit an oxygen reduction wave because of water reduction occurring at a more positive potential. For a pH 7 solution an oxygen wave is obtained with an elongated break having a half-wave potential of -0.52 V. At pH 10 the reduction becomes a double wave with the first wave having a half-wave potential of -0.32 V and the second wave having a half-wave potential of -0.60 V. The two waves at pH 12 have half-wave potentials of -0.31 V and -0.71 V, respectively, and are approximately equal in height. Thus, the first wave is independent of pH with an average value of -0.32 V while the second wave is pH-dependent with a half-wave potential which shifts more negatively about 0.06 V per pH unit. The latter wave indicates that one electron per hydroxide ion is involved in the reduction reaction. The independence of the first wave with respect to pH would indicate that oxygen may undergo direct reduction under the conditions of this wave.

Electrical oxidation of the tantalum did not appear to be effective; however, oxidation with a $\text{Ce}(\text{NO}_3)_4$ - HNO_3 solution gives a definite oxide coating. Oxygen reduction waves at the freshly formed tantalum oxide electrode were not reproducible and the reduction current appeared to be inhibited.

The tantalum electrode is similar to the nickel electrode with respect to the reduction of dissolved oxygen. However, for a nickel electrode it is possible to obtain

an essentially reduced electrode which is not possible with a tantalum electrode in aqueous solution. The ability to obtain a reduced form of an electrode is highly dependent upon the rate of formation and reduction of the oxide film. For the nickel electrode these factors make it possible to produce a reduced electrode, but they prevent such an electrode condition in the case of tantalum.

The tungsten electrode behaves erratically and has characteristics which indicate that it is only slowly oxidized and reduced. Therefore, the results for oxygen reduction with this electrode are not reproducible. Apparently, the electrode is somewhat similar to the tantalum electrode, but with a less inert oxide coating.

Chronopotentiometry of oxygen at platinum electrodes

The usefulness of chronopotentiometry for the study of electrode reactions has been amply reviewed^{14,15}. ANSON AND LINGANE^{16,17} have used the method to study the oxidation of iodide ion at platinum electrodes, and to establish that $\text{Pt}(\text{OH})_2$ and PtO_2 actually exist on the surface of platinum electrodes. ANSON¹³ has also applied the method to the study of the reduction of iodate ion at pre-oxidized and pre-reduced platinum electrodes.

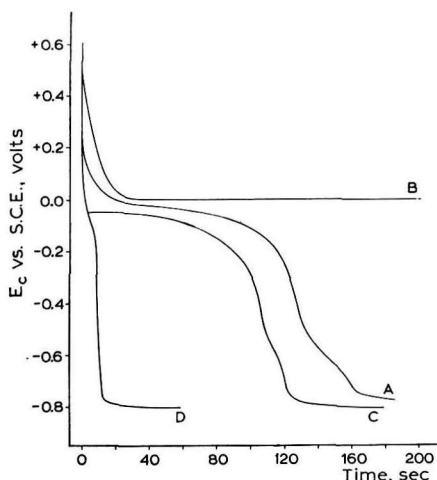
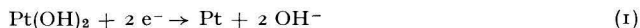


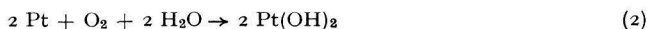
Fig. 4. Chronopotentiometric reductions at a platinum electrode. All solutions are 0.1 *F* in K_2SO_4 and are adjusted to pH 8. Curves A and D: reduction of $\text{Pt}(\text{OH})_2$; the electrode is pre-oxidized electrolytically followed by deaeration of the solution with pre-purified nitrogen. Current densities: curve A: 0.02 mA/cm^2 ; curve D: 0.30 mA/cm^2 . Curves B and C: reduction of oxygen in solution. Current densities: curve B: 0.02 mA/cm^2 ; curve C: 0.30 mA/cm^2 .

Fig. 4 shows chronopotentiograms for the reduction of the oxide film on a platinum electrode as well as for the reduction of dissolved oxygen at a platinum electrode. Studies of the effect of current density upon the chronopotentiograms confirm that the reduction wave is diffusion controlled. That is, $i\tau^{1/2}/C$ is equal to a constant, where i is the current density, τ is the transition time and C is the concentration of dissolved oxygen. The effect of pH on the quarter-wave potential for the oxide reduction as well as for the reduction of oxygen is shown by curves B and C in Fig. 1.

The quarter-wave potential for a chronopotentiogram is analogous to the half-wave potential of a voltammetric wave. Curve A in Fig. 1 is the half-wave potential for the reduction of oxygen at a pre-oxidized platinum electrode as a function of pH. Because of the almost identical character of the oxide reduction and the oxygen reduction, the electrode reaction must be the same for the two reductions. Thus, for the oxide film, the reduction reaction is



In the case of the oxygen reduction the first reaction is the reduction of the oxide film present on the electrode (reaction 1). Next the oxygen in solution reoxidizes the electrode,



which is in turn re-reduced by reaction 1.

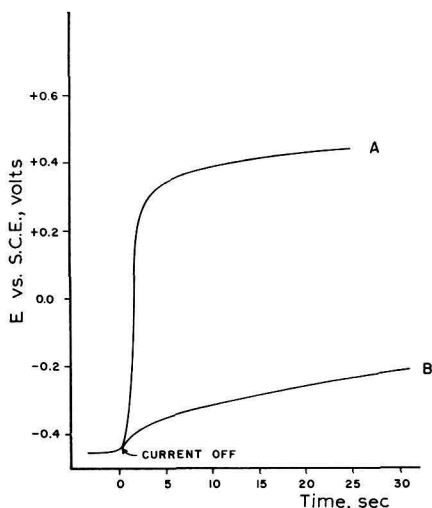


Fig. 5. Oxidation of a reduced platinum electrode by dissolved oxygen. The potential is plotted as function of time. The electrode is reduced electrolytically to the point indicated on the curves. All solutions are 0.1 *F* in K_2SO_4 and adjusted to pH 2. Curve A: for a solution saturated with oxygen at 1 atm. Curve B: for a solution deaerated with pre-purified nitrogen (prior to reduction of the electrode).

Fig. 5 gives additional evidence that reaction 2 actually occurs and indicates how fast the reaction goes. The curve represents the change in potential of a reduced platinum electrode when exposed to a dissolved oxygen solution.

If a platinum electrode is extensively reduced electrolytically at pH 2, a double wave is obtained for the chronopotentiometric reduction of oxygen. Usually it is first necessary to remove any old oxide film with aqua regia before starting the conditioning by repeated reduction. The preconditioning necessary is extensive, and even then the double wave is frequently not obtained. Such a double wave is shown in Fig. 6 (curve A). The first wave is identical to the wave observed for the reduction of $\text{Pt}(\text{OH})_2$.

However, the second wave has a quarter-wave potential of -0.16 V which corresponds to the half-wave potential of oxygen at a reduced platinum electrode.

Exhaustive reduction of a platinum electrode at pH 12 on occasion gives a double wave for oxygen reduction which is represented by curve B of Fig. 6. Again, the

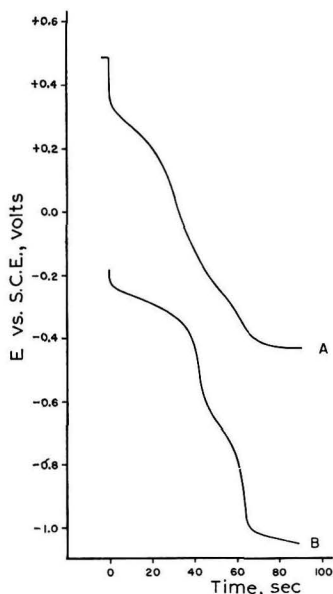


Fig. 6. Chronopotentiometric reductions of dissolved oxygen at pre-reduced platinum electrodes. The solutions are 0.1 F in K_2SO_4 and are saturated with oxygen at 1 atm. The current density for both curves is 0.50 mA/cm^2 . Curve A: solution adjusted to pH 2. Curve B: solution adjusted to pH 12.

first wave corresponds to the $\text{Pt}(\text{OH})_2$ reduction, but the second wave is much more negative and has a quarter-wave potential of -0.65 V and appears to be pH-dependent. This wave may represent the direct reduction of oxygen to OH^- ions.



The double wave is only obtained after repeated reduction of the platinum electrode, after first removing the oxide film with aqua regia. Such behavior indicates that the surface of the electrode may be undergoing considerable change. That the appearance of a double wave is truly due to the electrode surface, and not to a change in the solution, has been confirmed by placing a conditioned electrode in a fresh solution of dissolved oxygen. Under these conditions the electrode immediately exhibits the double wave. The conditioning process may actually cause the electrode surface to be polished such that additional active sites are provided. A sufficiently conditioned electrode may make it possible for reaction 3 to occur.

The relative transition times, τ , for the two waves (curve B, Fig. 6) are affected by both current density and concentration of oxygen. Table I shows the general

trends caused by variation of the two parameters, current density and partial pressure of dissolved oxygen. As the current density is increased the transition time for the second wave increases. Also, with a decrease in the partial pressure of dissolved oxygen the second transition time increases relative to that of the first wave. These observations support the conclusion that two processes are taking place at the electrode.

TABLE I

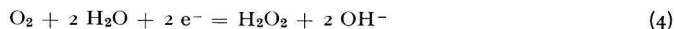
RATIO OF THE TRANSITION TIMES AT A PRECONDITIONED PLATINUM ELECTRODE FOR THE FIRST AND SECOND REDUCTION WAVES OF OXYGEN AS A FUNCTION OF CURRENT DENSITY AND PARTIAL PRESSURE OF OXYGEN

<i>Current density (mA/cm²)</i>	<i>Partial pressure of oxygen (atm)</i>	<i>Ratio of τ_1 to τ_2</i>
0.40	1.00	1 : 0.427
0.40	0.21	1 : 0.938
0.50	1.00	1 : 0.655
0.50	0.21	1 : 1.159
1.00	1.00	1 : 2.89
1.50	1.00	1 : 5.00
2.00	1.00	1 : 8.00

The first wave clearly corresponds to the reduction represented by eqn. (1). As the current density increases, or the partial pressure of oxygen decreases, a second electrode reaction is favored. Although many reactions could be proposed to account for a second wave, a reaction involving direct reduction of oxygen would seem to be favored. Thus, the reaction expressed by eqn. (3) appears reasonable. Production of hydrogen peroxide is unlikely because of its unstable character under the basic conditions of the solution, pH 12. Any peroxide formed undoubtedly immediately decomposes such that eqn. (3) represents the overall reduction reaction for the second wave. It is noteworthy that the quarter-wave potential for the second wave at pH 12 is -0.65 V. At this potential the platinum electrode is completely reduced to the metal and thus, eqn. (1), or some ramification of it, cannot be responsible for the second wave.

In an effort to support some of the conclusions concerning the reduction reactions at a platinum electrode, a series of electrolysis studies have been made at a 20 cm^2 platinum gauze electrode. The potential of the electrode relative to a reference electrode was controlled and the electrolysis current integrated to determine the number of coulombs supplied to the oxygen containing solution.

According to LAITINEN AND KOLTHOFF⁵ the reduction reaction for oxygen at a platinum electrode is



When the gauze electrode was pre-oxidized and used to electrolyze a pH 2, 0.1 F K_2SO_4 solution with an electrode potential of $+0.20$ V, the electrolysis produced only 7.3% of the theoretical amount of H_2O_2 calculated from the number of coulombs and eqn. (4). For the same electrode and solution conditions, but with the electrode held at -0.20 V, the electrolysis produced 10.0% of the theoretical amount of H_2O_2 . At pH 8 and with the electrode at -0.60 V, the electrolysis produced 5.9% of the theo-

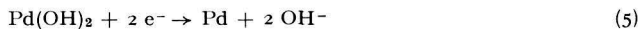
retical amount of H_2O_2 . However, if the electrode was carefully pre-reduced, then the electrolysis of a pH 2 solution at -0.1 to -0.2 V produced 30 to 50% of the theoretical amount of H_2O_2 . Furthermore, it has been established that the gauze electrode catalyzes the decomposition of H_2O_2 rather rapidly. Thus, the production of H_2O_2 is highly favored, possibly to the extent of almost 100%, at a reduced platinum electrode when the electrode potential is held at -0.1 to -0.2 V and the dissolved oxygen is present in an acidic solution. On the other hand, at a platinum oxide electrode or for basic solutions the formation of H_2O_2 from the reduction of dissolved oxygen is not favored. Some reduction reaction other than that indicated by eqn. (4) must be taking place. These observations lend support to the conclusion that eqn. 1 represents the electrode reaction for oxygen reduction at a pre-oxidized platinum electrode, and that eqn. (3) represents the electrode reaction for reduced electrode in basic solutions.

Several studies of the effects of changes of temperature and of oxygen partial pressure on the diffusion current have established that the current is diffusion controlled. This is true for all normal chronopotentiograms such as illustrated by the curves of Fig. 4. This confirms the earlier observation that $i\tau^{1/2}$ remains constant for a current density from 0.20 to 0.70 mA/cm² when the partial pressure of dissolved oxygen is 1 atm. The abnormal reduction of dissolved oxygen at platinum electrodes in the presence of CaCl_2 , which was observed for the voltammetric studies, was not observed in the case of the chronopotentiometric studies of oxygen at platinum electrodes.

Chronopotentiometry of oxygen at palladium electrodes

Reduction of dissolved oxygen at palladium electrodes has also been studied by chronopotentiometry. Again the effects of solution composition and preconditioning of the electrode surface have been the major variables considered.

The pre-oxidized form of a palladium electrode is easily made by immersion in a $\text{Ce}(\text{NO}_3)_4$ - HNO_3 solution or by electrolytic anodization. Chronopotentiometric reduction of this oxide film in the absence of dissolved oxygen gives a curve with two reduction waves, both having quarter-wave potentials which are pH-dependent. The first wave is concluded to be due to the reduction of PdO_2 while the second wave is due to the reduction of the $+2$ oxide.



Curve B of Fig. 2 represents the quarter-wave potential of the PdO_2 reduction as a function of pH, and curve C of Fig. 2 shows an analogous plot for the reduction expressed by eqn. (5).

A pre-oxidized palladium electrode in the presence of dissolved oxygen gives a chronopotentiogram similar in shape to that of the palladium oxide electrode. However, the second reduction step has a much larger transition time due to the presence of oxygen. Curve D of Fig. 2 represents the quarter-wave potential for the chronopotentiometric reduction of dissolved oxygen as a function of pH. The similarity between curve D, curve C, and curve A (voltammetric reduction of oxygen at a pre-oxidized electrode) indicates that the same electrode process is taking place in all three situations. Thus, the actual electrode reaction is expressed by eqn. 5, and in the presence of dissolved oxygen the electrode is re-oxidized to $\text{Pd}(\text{OH})_2$.

The slope of curve D also supports the conclusion that the reduction reaction is expressed by eqn. (5). In general the chronopotentiometric behavior of dissolved oxygen at a palladium electrode is quite similar to that at a platinum electrode. The double waves found at platinum electrodes were also observed at palladium electrodes under appropriate electrode and solution conditions.

With an unconditioned palladium electrode chronopotentiometric reduction of oxygen gives reduction curves which are also pH-dependent, but which are less reproducible than at the pre-oxidized electrode. Furthermore, the unconditioned electrode does not give a reduction plateau corresponding to the reduction of the higher oxide of palladium (curve B, Fig. 2). Apparently the PdO₂ is not present on the palladium electrode under normal conditions.

Chronopotentiometry of oxygen at nickel electrodes

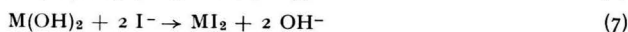
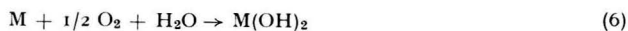
A pre-oxidized nickel electrode gives a double reduction wave in the absence of dissolved oxygen. Both of the reduction waves are pH-dependent, and undoubtedly correspond to reduction of the +4 and +2 oxides of nickel. In the presence of dissolved oxygen this pre-oxidized electrode gives a similar double wave with the first wave having the same transition time as in the absence of oxygen. However, the second wave has a much longer transition time corresponding to the reduction of the dissolved oxygen.

Curve F of Fig. 2 indicates the variation in quarter-wave potential for the reduction of dissolved oxygen as a function of pH. Studies of the variation in the reduction potentials for the +4 and +2 oxides at different pH's gave erratic results which were not reproducible. In the presence of dissolved oxygen the wave due to the +4 oxide remains together with a second wave for the reduction of oxygen. However, the mechanism of oxygen reduction is believed to be the same as it is at pre-oxidized platinum and palladium electrodes; namely, reduction of Ni(OH)₂ follow by re-oxidation of the electrode. The slope for curve F of Fig. 2 lends support to this conclusion.

Electrolytic reduction of oxygen in the presence of iodide ion

The reduction of dissolved oxygen at platinum, palladium and nickel electrodes is strongly affected by the presence of iodide ion in the electrolytic solutions. Voltammetric studies have shown that these three electrodes in potassium iodide solutions give oxygen reduction waves which are independent of pH, but which change with iodide ion concentration. Fig. 7 shows the change in half-wave (or quarter-wave) potential for oxygen reduction at these electrodes as a function of the negative logarithm of iodide concentration. Curves A, B and C are for voltammetric reduction at platinum, palladium and nickel electrodes, respectively. Curves D and E are for the chronopotentiometric reduction of oxygen at platinum and palladium electrodes, respectively.

Although pre-conditioning has an effect on the oxygen reduction waves in the presence of iodide ion, the variation of reduction potential with iodide concentration remains. The behavior of the three electrodes can be explained by a generalized mechanism



where M represents platinum, palladium and nickel. The slopes for the curves in Fig. 7 give support to the reaction sequence represented by eqns. 6, 7 and 8. Such a mechanism is particularly attractive for the platinum and palladium electrodes because of the insoluble character of PtI_2 and PdI_2 . This factor would favor the reac-

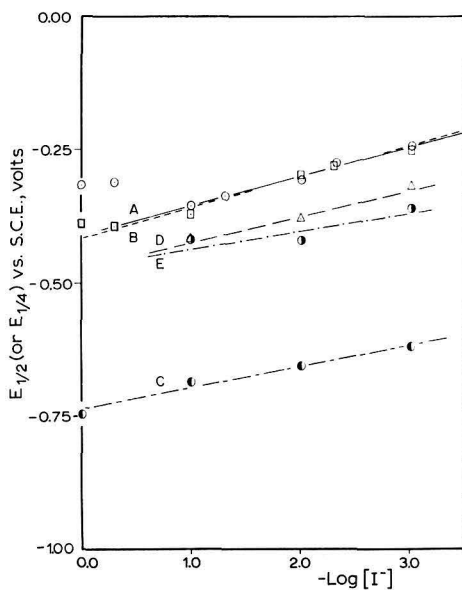


Fig. 7. Voltammetric and chronopotentiometric reduction of oxygen in the presence of iodide ion at platinum and palladium electrodes. The half-wave (voltammetric) and quarter-wave (chronopotentiometric) potentials as a function of $-\log(I^-)$. All solutions were adjusted to an ionic strength $0.1 M$ with K_2SO_4 . Curve A: \circ , voltammetric reduction of dissolved oxygen using an unconditioned platinum electrode; solution adjusted to pH 10; slope is equal to $-0.056 V$ per $-\log(I^-)$ unit. Curve B: \square , voltammetric reduction of dissolved oxygen using an unconditioned palladium electrode; solution adjusted to pH 10; slope is equal to $-0.059 V$ per $-\log(I^-)$ unit. Curve C: \bullet , voltammetric reduction of dissolved oxygen using an unconditioned nickel electrode; solution is unbuffered; slope is equal to $-0.40 V$ per $-\log(I^-)$ unit. Curve D: \triangle , chronopotentiometric reduction of dissolved oxygen at a platinum electrode; solution is unbuffered; current, $0.50 mA/cm^2$; slope is equal to $-0.034 V$ per $-\log(I^-)$ unit. Curve E: \bullet , chronopotentiometric reduction of dissolved oxygen at a palladium electrode; solution unbuffered; current, $0.50 mA/cm^2$; slope is equal to $-0.050 V$ per $-\log(I^-)$ unit.

tion expressed by eqn. 7. That these two electrodes actually have been metalized to PtI_2 and PdI_2 is supported by the observation that both electrodes exhibit a "memory effect." Thus, a platinum or palladium electrode which has been exposed to an iodide solution, when later placed in a K_2SO_4 solution free of iodide ion, will still show a large negative shift in the potential for oxygen reduction. This appears to be due to a film of PtI_2 and PdI_2 left on the electrode surface from the iodide solution. After electrolytic reduction of a dissolved oxygen solution, free of iodide ion, the electrodes revert back to conventional platinum and palladium electrodes.

The deviations from linearity for curves A and B of Fig. 7 at the higher concentrations of iodide are, in all probability, due to the formation of soluble iodide complexes of the PtI_2 and PdI_2 electrode films. The behavior of the nickel electrode in the presence of iodide ion is less easily explained, especially in view of the high solubility

of NiI₂. Curve C of Fig. 7 clearly indicates, however, that iodide ions do interact with the oxide film of the nickel electrode.

Chronopotentiometric studies of oxygen reduction in the presence of iodide ion at platinum and palladium electrodes give reduction curves with two waves. The first wave for either electrode is pH-independent, but its potential shifts with iodide concentration. The quarter-wave potentials for this first wave, as a function of the negative logarithm of iodide concentration, are represented by curves D and E of Fig. 7 for the platinum and palladium electrodes, respectively. The second wave for the platinum and palladium electrodes is independent of iodide concentration and occurs at a quarter-wave potential of -0.50 to -0.60 V for both electrodes. As suggested previously this second wave may be due to the direct reduction of oxygen as expressed by equation 3.

Efforts to observe chronopotentiometric reduction waves for PtI₂ and PdI₂ in oxygen-free solutions gave erratic results. However, under certain conditions drawn out reduction curves were obtained which were consistent with the reductions observed for oxygen-containing solutions. Formation of PtI₂ and PdI₂ on the electrode surface in the absence of dissolved oxygen apparently is quite difficult and is the cause of the difficulties.

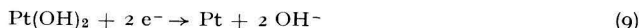
CONCLUSIONS

In the preceding section the conclusion is made that the reduction of dissolved oxygen at pre-oxidized platinum electrodes is a cyclic reaction. First, the Pt(OH)₂ on the electrode is reduced followed by re-oxidation of the electrode by the oxygen. The electrode is then re-reduced. The work of ANSON AND LINGANE¹⁷ has established conclusively that platinum electrodes have oxide coatings of Pt(OH)₂ and PtO₂. KOLTHOFF AND TANAKA¹⁸ also have given evidence for oxide films on platinum electrodes; HICKLING¹⁹ presented some of the first evidence for the existence of such Pt(OH)₂ films.

GINER²⁰ has suggested that the platinum electrode's behavior in solution is due to chemisorbed oxygen and not specific oxides. LAITINEN AND ENKE²¹ have also studied the oxide films on platinum electrodes. They concluded that the electrode is covered with a monolayer of oxide which can be regarded as equivalent to a chemisorbed oxygen atom layer. However, both of these groups were primarily concerned with acidic solutions, while our work has been directed to more basic systems.

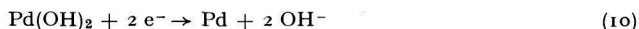
KOLTHOFF AND TANAKA¹⁹ tried to observe the oxidation of platinum by oxygen (eqn. (2)), but concluded the reaction did not take place. However, we have found that as the oxide film ages, it becomes increasingly difficult to reduce. Frequently it is necessary to resurface the electrode or to treat it with aqua regia in order to remove the initial oxide coating. The curve in Fig. 5 indicates how fast oxygen reacts with a freshly reduced electrode. Curve A in Fig. 4 illustrates how readily a fresh oxide film is reduced. Apparently in the work of KOLTHOFF AND TANAKA¹⁸ the electrode already had an old oxide film, and the oxygen was not capable of additional oxidation. BOCKRIS³ has noted that with time the attachment between Pt and O becomes stronger and reduction becomes less reversible.

On the basis of the data in Fig. 1, it is possible to determine a formal potential for the reaction



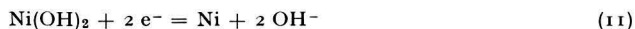
in the presence of 0.1 *F* K₂SO₄. The average of the values calculated from the curves in Fig. 1 is -0.14 V vs. N.H.E.

For analogous reasons the reduction of dissolved oxygen at pre-oxidized palladium electrodes appears to be due to a mechanism identical to that for the pre-oxidized platinum electrodes. Again, by using the data from Fig. 2 it is possible to determine the formal potential for the reaction



in the presence of 0.1 *F* K₂SO₄. The average for the values computed from Fig. 2 is -0.19 V vs. N.H.E.

The reduction of oxygen at a pre-oxidized nickel electrode apparently involves a mechanism similar to the pre-oxidized platinum and palladium electrodes. The more negative potential for specific pH's results from the more negative reduction potential of Ni(OH)₂. By using the data of Fig. 2 for the nickel electrode it is also possible to determine the formal potential for the reaction



in the presence of 0.1 *F* K₂SO₄. The average for the values computed from Fig. 2 is -0.74 V vs. N.H.E.

It seems reasonable to conclude that most metal electrodes which are oxidized by oxygen will behave in an analogous fashion. That is, the mechanism of reduction is the reduction of the metal oxide which is then reformed by the reaction of oxygen on the metal. The qualitative data for all of the metal electrodes except silver and gold support this conclusion. Furthermore, the data for the PtI₂, PdI₂, and NiI₂ electrode systems serve to support the general conclusion that oxygen is not directly reduced at pre-oxidized electrodes, but actually undergoes a cyclic reduction involving the electrode itself.

Platinum, palladium, nickel, gold and silver electrodes, when pre-reduced, give identical waves with a half-wave potential from -0.18 to -0.24 V. The first wave for oxygen reduction at a tantalum electrode, $E_{1/2} = -0.32$ V, probably also is due to the same reaction mechanism. The half-wave potentials for each of these electrodes is independent of pH. Apparently the reduction reaction at a reduced metal electrode is independent of electrode material. The almost identical half-wave potentials for oxygen reduction at all of the reduced electrodes support this conclusion. In order to prevent formation of a metal oxide and thus a different reduction mechanism, it is necessary to maintain the electrode at a potential more negative than the reduction potential of the metal oxide. Thus, the slow scan rates characteristic of voltammetry permit pre-reduction of the small amount of oxide formed by dissolved oxygen on the reduced electrode.

LAITINEN AND KOLTHOFF⁵ first showed that the reduction of oxygen at a platinum electrode is independent of pH, and also demonstrated that the electrode reaction produces hydrogen peroxide as a reduction product. That H₂O₂ is produced by the reduction of oxygen at reduced electrodes has been confirmed many times²⁻¹². Electrolytic production of H₂O₂ is favored at reduced electrode surfaces in acidic solutions, as shown by our data for oxygen reduction at platinum electrodes. In fact, very little H₂O₂ is produced at pre-oxidized electrodes.

AZZAM and co-workers¹² were the first group to propose a mechanism for the reduction of oxygen at a mercury electrode

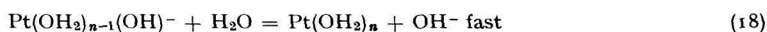


However, because the reduction wave is independent of pH, reaction 12 and 13 do not appear to be satisfactory. KOLTHOFF AND JORDAN⁷ give as a possible mechanism for the reduction of oxygen at a reduced gold electrode, the reactions



Although reaction 14 seems plausible, reaction 15 seems somewhat unlikely because of the repulsion of the electrode for the O_2^- ion. BAGOTSKII AND YABLOKOVA¹¹ suggested a reduction sequence similar to reactions 14 and 15.

It is desirable to take account of the hydrate layer which would be expected on the surface of the metal electrodes. Also, the proposed mechanism should be independent of pH, and if possible, should avoid the two-step reduction at the electrode required by reaction 8. With these considerations in mind and on the basis of our data, as well as that of others, we propose the following mechanism for the reduction of oxygen at reduced metal electrodes.



Reaction 17 is roughly analogous to reaction 14, but does take account of the hydrate layer on the electrode. Also the reduction is accomplished by hydrogen atom transfer rather than electron transfer. For reaction 19 LATIMER⁴ gives a ΔF° of -37.5 kcal, which suggests that this is a plausible reaction step and that it probably is a fast step. Analogous reactions can be written for other reduced metal electrodes.

EXPERIMENTAL

The voltammetric studies were made with a previously described²² polarograph which utilizes an X-Y recorder. This instrument has a voltage accuracy of ± 0.005 V and a current accuracy of $\pm 0.3\%$. In order to permit the recording of potential-current curves in both directions, the original instrument has been modified by replacing the spandrive motor with a reversible motor. Much of the half-wave potential data represent the average of a forward and reverse recording of the potential-current curve.

The electrolysis cell consisted of a modified H-cell²³ with a salt bridge which could be flushed and filled with an inert electrolyte. Thus, the salt bridge could be flushed periodically to prevent contamination of the reference electrode.

The various metal electrodes for the voltammetric studies were made in two ways. The platinum electrodes were prepared by sealing platinum wire, 0.12 mm in diameter, into the end of 5 mm soft glass tubing. The end of the electrode was then ground flush with the glass surface by using emery paper. All of the other electrodes were prepared

by using deKotinsky cement to seal the metal wire, 0.1 to 0.2 mm in diameter, into the end of 5 mm pyrex glass tubing. The latter electrodes were also ground flush with the cement by using emery paper. In general the electrodes were conditioned after construction by anodization and cathodization. The anodization was usually conducted at an applied voltage of 3 V, while cathodization was done with an applied voltage of approximately 1 V. The cathode for anodizations and the anode for cathodizations were both platinum foil electrodes. Oxide films on the various electrodes were also produced by immersion of the electrode in a $\text{Ce}(\text{NO}_3)_4$ - HNO_3 solution for several minutes (0.1 F $\text{Ce}(\text{NO}_3)_4$ and 1 F HNO_3).

The chronopotentiometric studies were made with an instrument constructed from Philbrick operational amplifiers. The design, construction and performance of this type of chronopotentiograph has been discussed by DEFORD²⁴. Any electrolysis current from 0.1 μA to 25 mA can be used with an accuracy of $\pm 0.1\%$. A Varian GII-A 10 mV strip-chart recorder with chart speeds of 1 and 4 inches per minute was used for recording the voltage-time curves. The recorded voltages are accurate to at least ± 0.02 V.

The electrolysis cell for the chronopotentiometric measurements was prepared by cutting the upper rim off of a 200-ml tall-form beaker. A rubber stopper was drilled to accommodate the reference electrode (a double-junction saturated calomel electrode with a saturated K_2SO_4 bridge), the working electrode (1 cm^2 in area in each side), and the auxiliary electrode (a platinum gauze electrode having an area of 20 cm^2). The working electrodes were fabricated by welding metal foil to 0.1 to 0.2 mm wire and sealing the metal wire into the end of 5 mm glass tubing in a manner analogous to the voltammetric electrodes. Additional holes were drilled to provide for flushing the cell with gases, both above and below the surface of the solution, and for the introduction of a glass electrode.

Pre-purified nitrogen was used for deaerating all solutions. All measurements were made at 25.0° unless otherwise indicated, using a thermostated bath which was regulated to $\pm 0.05^\circ$. The electrodes were fabricated from reagent-grade metal wire and foil. All other chemicals were also reagent grade; the oxygen gas having a purity of 99.6%.

pH measurements were made either with a Leeds and Northrup line operated pH-meter or a Beckman Model G pH-meter. Both instruments were standardized with standard buffers and were equipped with glass electrodes capable of being used in high pH solutions.

The solutions were analyzed for hydrogen peroxide using the spectrophotometric procedure suggested by ALLEN²⁵. A standard permanganate solution was used as a blank against a water reference. For an analysis the sample solution was added to a permanganate solution which, when diluted, would have initially had the same permanganate concentration as the blank. The decrease in absorbance of the permanganate absorption peak was directly proportional to the amount of hydrogen peroxide in the sample solution.

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SUMMARY

The reduction of dissolved oxygen has been studied at Pt, Pd, Ni, Ag, Au, Ta, W, Cu and Pb electrodes. Voltammetric and chronopotentiometric studies have established the effect of supporting electrolyte, solution-pH and electrode preconditioning upon the electrode reactions. Oxygen reduction at pre-oxidized metal electrodes is pH-dependent; for the Pt, Pd and Ni electrodes the electrode reaction for oxygen reduction is $M(OH)_2 + 2 e^- \rightarrow M + 2 OH^-$. The oxygen in solution re-oxidizes the electrode which is then re-reduced. The reduction of oxygen at all pre-oxidized metal electrodes except Ag and Au appears to occur by the same mechanism. The half-wave potential for oxygen reduction at pre-reduced metal electrodes is -0.18 to -0.24 V vs. S.C.E. and is independent of pH; hydrogen peroxide is the primary reduction product. A sequence of reactions is proposed to account for the formation of H_2O_2 in acidic solutions by a pH-independent mechanism. Potassium iodide causes the reduction of oxygen to become pH-independent at Pt, Pd and Ni electrodes; the potential for reduction becomes dependent, however, upon iodide concentration. The formal reduction potentials for the Pt(OH)₂, Pd(OH)₂ and Ni(OH)₂ electrodes in 0.1 F K₂SO₄ have been evaluated; the average values are -0.14 , -0.19 and -0.74 V vs. N.H.E., respectively.

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

III. CAS DE PLUSIEURS RÉACTIONS DE DÉCHARGE DIRECTE SUCCESSIVES ET CAS D'UNE RÉACTION DE DÉCHARGE EN PLUSIEURS ÉTAPES CONSÉCUTIVES

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INTRODUCTION

Deux publications antérieures^{1,2} ont été consacrées à définir les principales caractéristiques de la méthode électroanalytique où le courant imposé est de la forme $i = q\sqrt{t}$ (q étant le facteur d'amplitude, maintenu constant pour une expérience donnée). On y a notamment montré que les temps de transition sont, pour une substance dépolarisante donnée, proportionnels à sa concentration analytique.

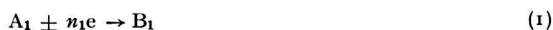
L'objet de cette communication est d'étendre la théorie de la méthode au cas où la solution contient plusieurs espèces électroactives ("consecutive reactions"), et à celui où la décharge d'une substance unique met en jeu un nombre d'électrons différent selon la valeur de la tension d'électrode ("stepwise reactions"). Des cas analogues ont déjà été traités par DELAHAY ET BERZINS³ pour la méthode chronopotentiométrique à courant constant.

Pour simplifier la résolution mathématique, on supposera que la diffusion procède en régime linéaire et que les composantes d'apport par migration et convection sont annulées par les procédés classiques (présence d'un large excès d'électrolyte support, si les particules dépolarisantes sont chargées; absence d'agitation; durée d'électrolyse relativement brève; géométrie appropriée de la cellule). Par ailleurs, la fraction du courant consommée par la charge capacitive de l'interphase est tenue pour négligeable. Enfin, la solution est initialement homogène.

CAS DE PLUSIEURS RÉACTIONS DE DÉCHARGE SUCCESSIVES

Formulation du problème et conditions limites et initiales dans le cas de deux réactions de décharge successives

On envisage le cas de deux réactions simples procédant par décharge directe à l'électrode. Soit



Les diverses particules sont toutes supposées solubles; τ_1 et τ_2 représentent respectivement les temps de transition relatifs aux processus (1) et (2).

a_1, a_2, b_1, b_2 sont respectivement les concentrations des espèces, A_1, A_2, B_1, B_2 exprimées en mol cm^{-3} et $D_{A_1}, D_{A_2}, D_{B_1}, D_{B_2}$ sont les coefficients de diffusion correspondants en $\text{cm}^2 \text{sec}^{-1}$.

La réaction (1) procède seule jusqu'au temps τ_1 . Dans l'intervalle $0-\tau_1$ la distribution des concentrations a_1 est indépendante de la présence des particules A_2 . On a par conséquent¹

$$a_1(x, t^0) = a_1^0 - \frac{q}{2 n_1 F D_{A_1}} \left\{ \sqrt{\pi D_{A_1}} \left(t^0 + \frac{x^2}{2 D_{A_1}} \right) \text{cfer} \left(\frac{x}{2 \sqrt{D_{A_1} t^0}} \right) - x \sqrt{t^0} \exp \left(-\frac{x^2}{4 D_{A_1} t^0} \right) \right\} \quad (3)$$

où cfer désigne le complément de la fonction d'erreur, x la distance (en cm) mesurée à partir de l'électrode, F le faraday, q le facteur d'amplitude (en $\text{A cm}^{-1} \text{sec}^{-1/2}$) et a_1^0 la concentration de A_1 au sein de la solution. Le temps t^0 a pour origine le début de la mesure. Au temps τ_1 , la concentration a_1 s'annule à l'électrode, et

$$a_1^0 = \frac{q}{2 n_1 F} \sqrt{\frac{\pi}{D_{A_1}}} \tau_1 \quad (4)$$

Dès lors, si l'on compte les temps t à partir du temps de transition τ_1 , soit

$$t = t^0 - \tau_1 \quad (5)$$

on peut écrire les conditions initiales

$$a_1(x, 0) = a_1^0 - \frac{q}{2 n_1 F D_{A_1}} \left\{ \sqrt{\pi D_{A_1}} \left(\tau_1 + \frac{x^2}{2 D_{A_1}} \right) \text{cfer} \left(\frac{x}{2 \sqrt{D_{A_1} \tau_1}} \right) - x \sqrt{\tau_1} \exp \left(-\frac{x^2}{4 D_{A_1} \tau_1} \right) \right\} \quad (6)$$

$$a_2(x, 0) = a_2^0 \quad (7)$$

$$b_2(x, 0) = 0 \quad (8)$$

Au delà du temps de transition τ_1 la relation (3) n'est plus valable. En effet, la décharge des particules A_1 et A_2 consomme alors simultanément le courant; le flux à l'électrode est par conséquent donné par la condition

$$n_1 F D_{A_1} \left(\frac{\partial a_1(x, t)}{\partial x} \right)_{x=0} + n_2 F D_{A_2} \left(\frac{\partial a_2(x, t)}{\partial x} \right)_{x=0} = q \sqrt{\tau_1 + t} \quad (9)$$

Les autres conditions limites sont déterminées par le fait que a_1 reste nul au plan d'électrode, soit

$$a_1(0, t) = 0 \quad (10)$$

et par la relation

$$D_{A_2} \left(\frac{\partial a_2(x,t)}{\partial x} \right)_{x=0} + D_{B_2} \left(\frac{\partial b_2(x,t)}{\partial x} \right)_{x=0} = 0 \quad (11)$$

Il résulte enfin des conditions de semi-infinité que

$$a_1(\infty, t) = a_1^0 \quad (12)$$

$$a_2(\infty, t) = a_2^0 \quad (13)$$

$$b_2(\infty, t) = 0 \quad (14)$$

où a_2^0 est la concentration de A_2 au coeur de la solution.

Solution du problème

Le problème peut être résolu en deux étapes de calcul. Dans la première, on procède à l'intégration de l'équation différentielle seconde de FICK

$$\frac{\partial a_1(x,t)}{\partial t} = D_{A_1} \left(\frac{\partial^2 a_1(x,t)}{\partial x^2} \right) \quad (15)$$

pour des temps supérieurs à $\tau_1 (t \geq 0)$. Cette opération s'effectue en considérant les conditions (6), (10) et (12). Le calcul conduit à la valeur de

$$\left(\frac{\partial a_1(x,t)}{\partial x} \right)_{x=0}$$

qui permet ensuite avec les conditions (7), (8), (9), (11), (13) et (14) d'intégrer les équations de FICK pour les particules A_2 ,

$$\frac{\partial a_2(x,t)}{\partial t} = D_{A_2} \frac{\partial^2 a_2(x,t)}{\partial x^2} \quad (16)$$

et B_2 .

Dérivation de $(\partial a_1(x,t)/\partial x)_{x=0}$. L'équation (15) se résout à l'aide des transformées de Laplace définies par⁴

$$\bar{f}(s) = \int_0^{\infty} f(t) \exp(-st) dt \quad (17)$$

On obtient l'équation „subsidiare”

$$\frac{d^2 \bar{a}_1(x,s)}{dx^2} - \frac{s}{D_{A_1}} \bar{a}_1(x,s) = - \frac{a_1(x,0)}{D_{A_1}} \quad (18)$$

dont la solution est de la forme

$$\bar{a}_1(x,s) = M \exp\left(\sqrt{\frac{s}{D_{A_1}}} x\right) + N \exp\left(-\sqrt{\frac{s}{D_{A_1}}} x\right) + \bar{a}_{1p}(x,s) \quad (19)$$

M et N sont deux constantes tandis que \bar{a}_{1p} représente la solution particulière provenant de la non homogénéité de (18). On a

$$\bar{a}_{1p}(x,s) = \frac{1}{2\pi j} \int_{\gamma-j\infty}^{\gamma+j\infty} \frac{\bar{\Phi}(p)}{p^2 - \frac{s}{D_{A_1}}} \exp(px) dp \quad (20)$$

où γ est une constante positive, j l'imaginaire et

$$\frac{\bar{\Phi}(p)}{p^2 - \frac{s}{D_{A_1}}}$$

la transformée pour p sur la variable x de la solution de l'équation „subsidaire” (18). $\bar{\Phi}(p)$ représente par conséquent la transformée pour p de la fonction

$$-\frac{a_1(x,0)}{D_{A_1}}$$

La transformée inverse exprimée par l'intégrale (20) peut encore être évaluée grâce au théorème de convolution⁵ et en tenant compte de ce que la transformée inverse de

$$\frac{1}{p^2 - \frac{s}{D_{A_1}}}$$

vaut⁴

$$\sqrt{\frac{D_{A_1}}{s}} \sinh\left(\sqrt{\frac{s}{D_{A_1}}} x\right)$$

Soit

$$\bar{a}_{1p}(x,s) = \int_0^x \Phi(\eta) \sqrt{\frac{D_{A_1}}{s}} \sinh\left[\sqrt{\frac{s}{D_{A_1}}}(x-\eta)\right] d\eta \quad (21)$$

ou encore

$$\bar{a}_{1p}(x,s) = - \int_0^x \frac{a_1(\eta,0)}{\sqrt{D_{A_1}s}} \sinh\left[\sqrt{\frac{s}{D_{A_1}}}(x-\eta)\right] d\eta \quad (22)$$

La résolution de cette intégrale dans laquelle $a_1(\eta, 0)$ est donné par (6) s'effectue principalement par partie. On a finalement après un calcul assez long

$$\begin{aligned} \bar{a}_1(x, s) = & \frac{a_1}{s} + M' \exp\left(\sqrt{\frac{s}{D_{A_1}}} x\right) + N' \exp\left(-\sqrt{\frac{s}{D_{A_1}}} x\right) \\ & + \frac{\varrho}{2n_1 F D_{A_1} s} \left\{ x\sqrt{\tau_1} \exp\left(-\frac{x^2}{4D_{A_1}\tau_1}\right) - \sqrt{D_{A_1}\tau_1} \left(\tau_1 + \frac{x^2}{2D_{A_1}} + \frac{1}{s}\right) \operatorname{cfer}\left(\frac{x}{2\sqrt{D_{A_1}\tau_1}}\right) \right\} \\ & + \frac{\varrho\sqrt{\pi}}{4n_1 F \sqrt{D_{A_1}} s^2} \exp\left(s\tau_1 + \sqrt{\frac{s}{D_{A_1}}} x\right) \operatorname{cfer}\left(\frac{x}{2\sqrt{D_{A_1}\tau_1}} + \sqrt{s\tau_1}\right) \\ & + \frac{\varrho\sqrt{\pi}}{4n_1 F \sqrt{D_{A_1}} s^2} \exp\left(s\tau_1 - \sqrt{\frac{s}{D_{A_1}}} x\right) \operatorname{cfer}\left(\frac{x}{2\sqrt{D_{A_1}\tau_1}} - \sqrt{s\tau_1}\right) \end{aligned} \quad (23)$$

La condition (12) impose $M' = 0$ tandis que la valeur de N' est déterminée grâce à (10). On obtient alors

$$\left(\frac{\partial \bar{a}_1(x, s)}{\partial x}\right)_{x=0} = \frac{\varrho}{2n_1 F D_{A_1}} \left\{ -\frac{\sqrt{\pi}}{s^{3/2}} + \frac{\sqrt{\pi}}{s^{3/2}} \exp(s\tau_1) \operatorname{cfer}\left(\sqrt{s\tau_1}\right) + \frac{2\sqrt{\tau_1}}{s} \right\} \quad (24)$$

L'évaluation de la transformée inverse de

$$\frac{\sqrt{\pi}}{s^{3/2}} \exp(s\tau_1) \operatorname{cfer}\left(\sqrt{s\tau_1}\right)$$

résulte du théorème de convolution et de la transformée inverse de

$$\frac{\sqrt{\pi}}{s^{1/2}} \exp(s\tau_1) \operatorname{cfer}\left(\sqrt{s\tau_1}\right), \text{ soit } \frac{1}{\sqrt{\tau_1 + t}}.$$

On a⁵

$$\int_0^t \frac{d\xi}{\sqrt{\tau_1 + \xi}} = 2(\sqrt{\tau_1 + t} - \sqrt{\tau_1}) \quad (25)$$

et par conséquent

$$\left(\frac{\partial a_1(x, t)}{\partial x}\right)_{x=0} = \frac{\varrho}{n_1 F D_{A_1}} \left\{ \sqrt{\tau_1 + t} - \sqrt{t} \right\} \quad (26)$$

Cette relation établit la loi suivant laquelle le flux des particules A_1 se déchargeant à l'électrode diminue en fonction du temps écoulé depuis τ_1 ($a_1(0, t) = 0$).

Détermination de $a_2(x, t)$ et $b_2(x, t)$. La condition (9) donne avec (26)

$$\left(\frac{\partial a_2(x, t)}{\partial x}\right)_{x=0} = \frac{\varrho}{n_2 D_{A_2} F} \sqrt{t} \quad (27)$$

Cette valeur du flux à l'électrode, ainsi que les conditions initiales (7) et de semi-infinité (13) ramènent la résolution de l'équation (16) aux calculs effectués antérieurement pour la réaction de décharge directe isolée (*cf.* appendice de la référence 1). Il en est de même pour la distribution des concentrations $b_2(x,t)$ qui obéit aux conditions initiales et aux limites (8), (11) et (14).

La concentration $a_2(x,t)$ est donnée par la relation (3) dans laquelle on substitue t à t^0 , a_2^0 à a_1^0 , n_2 à n_1 et D_{A_2} à D_{A_1} . A la surface de l'électrode

$$a_2(0,t) = a_2^0 - \frac{qt}{2n_2F} \sqrt{\frac{\pi}{D_{A_2}}} \quad (28)$$

$$b_2(0,t) = \frac{qt}{2n_2F} \sqrt{\frac{\pi}{D_{B_2}}} \quad (29)$$

Au temps de transition τ_2 (compté à partir de τ_1)

$$a_2(0,t) = 0 \quad (30)$$

et dès lors

$$a_2^0 = \frac{q\tau_2}{2n_2F} \sqrt{\frac{\pi}{D_{A_2}}} \quad (31)$$

On peut conclure de (31) et de (4) que le rapport τ_1/τ_2 s'exprime de manière particulièrement simple par la relation

$$\frac{\tau_1}{\tau_2} = \frac{a_1^0 n_1 \sqrt{D_{A_1}}}{a_2^0 n_2 \sqrt{D_{A_2}}} \quad (32)$$

d'où il résulte que

$$\frac{a_2^0 n_2 \sqrt{D_{A_2}} + a_1^0 n_1 \sqrt{D_{A_1}}}{a_1^0 n_1 \sqrt{D_{A_1}}} = \frac{\tau_1 + \tau_2}{\tau_1} \quad (33)$$

Discussion et extension du problème au cas où le nombre des décharges successives est quelconque

1. La relation (32) donnant le rapport des temps de transition est formellement identique à celle qui lie les courants de diffusion polarographiques du système considéré. Dans les deux cas, il y a additivité des grandeurs mesurées. Cette caractéristique de la méthode a été vérifiée pour la réduction du cadmium et du zinc (à des concentrations comprises entre $0.8 \cdot 10^{-5} M$ et $2 \cdot 10^{-4} M$) en tampon ammoniacal (NH_4OH , $0.1 M$; $(\text{NH}_4)_2\text{SO}_4$, $0.25 M$) et en présence de sulfite (Na_2SO_3 , $0.1 M$). La valeur trouvée pour le rapport $\sqrt{D_{A_1}/D_{A_2}}$ (Fig. 1) est en excellent accord avec la valeur correspondante (Fig. 2) déterminée par voie polarographique.

2. Il est intéressant de noter d'autre part que la variation des concentrations a_2 et b_2 rapportée au temps écoulé depuis τ_1 est analogue à la distribution calculée pour a_1 et b_1 dans l'intervalle de temps compris entre le début de la mesure et τ_1 . Les flux des diverses particules se superposent donc de telle sorte que tout se passe comme si A_2 était seul en solution à partir de l'instant τ_1 compté alors comme nouvelle origine des temps. En d'autres termes, le courant non consommé par la décharge de A_1 obéit à la relation particulièrement simple $i = \rho\sqrt{t^0 - \tau_1}$.

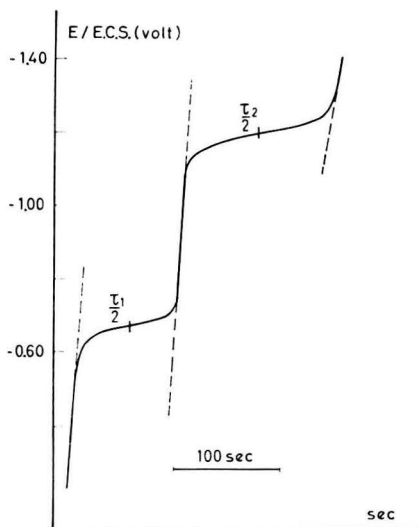


Fig. 1. Réduction du cadmium et zinc en tampon ammoniacal, par la méthode chronopotentiométrique en $i = \rho\sqrt{t}[\tau_1/\tau_2] = 0.70 \pm 0.01$; $[\text{Cd}^{2+}] = [\text{Zn}^{2+}] = 2 \cdot 10^{-4} M$; $\rho = 0.894 \cdot 10^{-6} \text{ A cm}^{-2} \text{ sec}^{\frac{1}{2}}$.

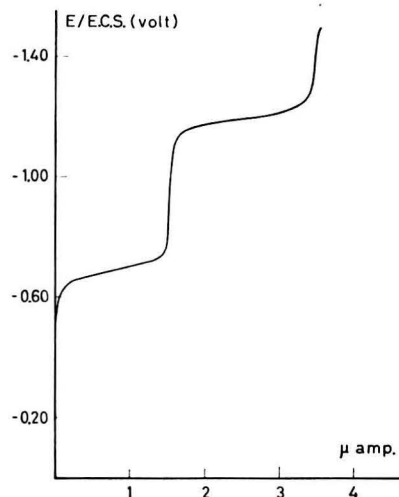


Fig. 2. Réduction du cadmium et zinc en tampon ammoniacal par polarographie ($i_{\text{Cd}^{2+}}/i_{\text{Zn}^{2+}} = 0.70 \pm 0.01$); $[\text{Cd}^{2+}] = [\text{Zn}^{2+}] = 2 \cdot 10^{-4} M$.

Il résulte de cette propriété et plus particulièrement des conditions (28) et (29) que l'équation des courbes de polarisation tension d'électrode-temps pour un processus de décharge et une valeur donnée de ρ est indépendante du fait que cette réaction est précédée ou non d'une autre. L'allure des chronopotentiogrammes est la résultante additive de deux courbes de polarisation isolées, sans qu'il survienne de distorsion en amplitude ou en morphologie. L'analogie avec la méthode polarographique est donc complète.

3. On peut aisément étendre le traitement théorique au cas où il a y plus de deux réactions à considérer. La résolution du problème de transfert massique relatif à la $q^{\text{ième}}$ réaction est en effet ramenée au calcul effectué pour a_2 et b_2 , avec comme origine le temps $\tau_1 + \tau_2 \dots + \tau_{q-1}$. On a ainsi:

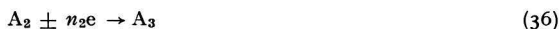
$$\frac{\tau_m}{\tau_q} = \frac{a_m^0 n_m \sqrt{D_{Am}}}{a_q^0 n_q \sqrt{D_{Aq}}} \quad (34)$$

où m est un nombre entier tel que $1 \leq m \leq q$.

CAS D'UNE DÉCHARGE PROCÉDANT EN PLUSIEURS ÉTAPES CONSÉCUTIVES

Formulation du problème et conditions limites et initiales dans le cas de deux étapes consécutives

On choisit le cas de deux réactions consécutives procédant par décharge directe à des tensions d'électrode différentes, soit



Les diverses particules sont supposées solubles, τ_1 et τ_2 sont respectivement les temps de transition correspondant aux étapes (35), (36); a_1 , a_2 et a_3 représentent respectivement les concentrations en mol cm^{-3} et D_{A_1} , D_{A_2} , D_{A_3} les coefficients de diffusion des espèces A_1 , A_2 et A_3 .

Jusqu'au temps de transition τ_1 les particules A_1 se déchargent à l'électrode à l'intervention de la seule réaction (35). Les concentrations a_1 sont alors données par l'équation (3), le temps t^0 ayant pour origine l'enclenchement du courant. Si l'on adopte à présent le temps t défini par la relation (5), la distribution initiale, c'est-à-dire au temps τ_1 , des concentrations a_1 est fournie par la relation (6), tandis que l'on a pour a_2 et a_3

$$a_2(x, 0) = \frac{q}{2n_1 F D_{A_2}} \left\{ \sqrt{\pi D_{A_2}} \left(\tau_1 + \frac{x^2}{2D_{A_2}} \right) \text{cfer} \left(\frac{x}{2\sqrt{D_{A_2}\tau_1}} \right) - x\sqrt{\tau_1} \exp \left(-\frac{x^2}{4D_{A_2}\tau_1} \right) \right\} \quad (37)$$

$$a_3(x, 0) = 0 \quad (38)$$

Dès le moment τ_1 , la concentration a_1 est nulle à l'électrode (10) et le courant est assuré simultanément par la décharge (36) des particules A_2 produites par la réaction (35) depuis le début de la mesure et par cette dernière réaction.

Il s'ensuit que le courant instantané vaut

$$(n_1 + n_2) F D_{A_1} \left(\frac{\partial a_1(x, t)}{\partial x} \right)_{x=0} + n_2 F D_{A_2} \left(\frac{\partial a_2(x, t)}{\partial x} \right)_{x=0} = q\sqrt{\tau_1 + t} \quad (39)$$

Enfin, on a, pour l'ensemble des flux de matière à l'électrode,

$$D_{A_1} \left(\frac{\partial a_1(x, t)}{\partial x} \right)_{x=0} + D_{A_2} \left(\frac{\partial a_2(x, t)}{\partial x} \right)_{x=0} + D_{A_3} \left(\frac{\partial a_3(x, t)}{\partial x} \right)_{x=0} = 0 \quad (40)$$

La relation (12) et

$$a_2(\infty, t) = 0 \quad (41)$$

$$a_3(\infty, t) = 0 \quad (42)$$

satisfont à la condition de semi-infinité.

Solution du problème

L'intégration de l'équation de FICK (15) pour $t \geq 0$ s'effectue en utilisant les conditions (6), (10) et (12). Le calcul est en tout point semblable à celui décrit précédemment pour le cas des réactions de décharge successives. On trouve ainsi la relation (26), c'est-à-dire la valeur du courant partiel correspondant à la réaction (35). Cette dernière expression ainsi que les conditions (37)–(42) permettent de résoudre l'équation de FICK pour les particules A_2 (16) et A_3 .

Détermination de $a_2(x,t)$ et $a_3(x,t)$. L'équation (16) se résout de la même façon que (15). La solution de l'équation „subsidaire” est de la forme

$$\bar{a}_2(x,s) = P \exp\left(-\sqrt{\frac{s}{D_{A_2}}} x\right) + Q \exp\left(\sqrt{\frac{s}{D_{A_2}}} x\right) + \bar{a}_{2_p}(x,s) \quad (43)$$

P et Q sont des constantes d'intégration et \bar{a}_{2_p} est la solution particulière qui vaut⁵

$$\bar{a}_{2_p}(x,s) = - \int_0^x \frac{a_2(\eta,0)}{\sqrt{D_{A_2}s}} \sinh\left[\sqrt{\frac{s}{D_{A_2}}}(x-\eta)\right] d\eta \quad (44)$$

$a_2(\eta,0)$ est défini par la relation (37).

La résolution de (44) s'effectue par partie. On obtient enfin

$$\begin{aligned} \bar{a}_2(x,s) = & P' \exp\left(-\sqrt{\frac{s}{D_{A_2}}} x\right) + Q' \exp\left(\sqrt{\frac{s}{D_{A_2}}} x\right) \\ & - \frac{q}{2n_1FD_{A_2}s} \left\{ x\sqrt{\tau_1} \exp\left(-\frac{x^2}{4D_{A_2}\tau_1}\right) - \sqrt{\pi D_{A_2}} \left(\tau_1 + \frac{x^2}{2D_{A_2}} + \frac{1}{s}\right) \operatorname{cfer}\left(\frac{x}{2\sqrt{D_{A_2}\tau_1}}\right) \right. \\ & - \frac{q\sqrt{\pi}}{4n_1F\sqrt{D_{A_2}s^2}} \exp\left(s\tau_1 + \sqrt{\frac{s}{D_{A_2}}} x\right) \operatorname{cfer}\left(\frac{x}{2\sqrt{D_{A_2}\tau_1}} + \sqrt{s\tau_1}\right) \\ & \left. - \frac{q\sqrt{\pi}}{4n_1F\sqrt{D_{A_2}s^2}} \exp\left(s\tau_1 - \sqrt{\frac{s}{D_{A_2}}} x\right) \operatorname{cfer}\left(\frac{x}{2\sqrt{D_{A_2}\tau_1}} - \sqrt{s\tau_1}\right) \right\} \quad (45) \end{aligned}$$

La condition (41) impose Q' égal à zéro. La condition (39) devient avec (26)

$$n_2FD_{A_1} \left(\frac{\partial a_1(x,t)}{\partial x}\right)_{x=0} + n_2FD_{A_2} \left(\frac{\partial a_2(x,t)}{\partial x}\right)_{x=0} = q\sqrt{t} \quad (46)$$

La transformée de Laplace de cette relation donne, si l'on tient compte de (24)

$$\left(\frac{\partial \bar{a}_2(x,s)}{\partial x}\right)_{x=0} = \frac{\varrho\sqrt{\pi}}{2 n_2 F D_{A_2} s^{3/2}} - \frac{\varrho}{2 n_1 F D_{A_2}} \left(-\frac{\sqrt{\pi}}{s^{3/2}} + \frac{\sqrt{\pi}}{s^{3/2}} \exp(s\tau_1) \operatorname{cfer}(\sqrt{s\tau_1}) + \frac{2\sqrt{\tau_1}}{s}\right) \quad (47)$$

La condition (47) appliquée à (45) permet de déterminer P' et l'on obtient $a_2(0,t)$ après transformation inverse pour $x = 0$.

Grâce aux conditions (38), (40) et (42) et à la relation (46) l'évaluation de $a_3(x,t)$ est semblable à celle de $b_2(x,t)$ dans le cas précédent. La distribution des concentrations a_3 est alors représentée par l'expression (37) où l'on substitue t à τ_1 , n_2 à n_1 et D_{A_3} à D_{A_2} .

On a dès lors

$$a_2(0,t) = \frac{\varrho}{2n_1F} \sqrt{\frac{\pi}{D_{A_2}}} \tau_1 - \frac{\varrho}{2n_2F} \sqrt{\frac{\pi}{D_{A_2}}} t \quad (48)$$

et

$$a_3(0,t) = \frac{\varrho}{2n_2F} \sqrt{\frac{\pi}{D_{A_2}}} t \quad (49)$$

Au temps de transition τ_2 , $a_2(0,t)$ est nul ce qui conduit au rapport des temps de transition

$$\frac{\tau_1}{\tau_2} = \frac{n_1}{n_2} \quad (50)$$

et donne une expression équivalente à (48)

$$a_2(0,t) = \frac{\varrho}{2n_2F} \sqrt{\frac{\pi}{D_{A_2}}} (\tau_2 - t) \quad (51)$$

Discussion et généralisation du problème pour une réaction de décharge à nombre quelconque d'étapes consécutives

1. De même que dans le cas précédemment traité des réactions de décharge successives, la valeur du rapport τ_1/τ_2 est égale au rapport des courants de diffusion polarographiques du système étudié. Cette conséquence a été vérifiée expérimentalement à partir des deux ondes de réduction de l'oxygène, mesurées en milieu NaClO_4 , 0.4 M (Fig. 3).

2. On remarque par ailleurs que la concentration de A_2 à l'électrode (51) décroît de manière en tout point identique à celle de A_1 et de n'importe quelle particule se déchargeant en une seule étape¹. Cette conséquence résulte de la relation (46), qui exprime le fait que les particules A_2 créées depuis le début de l'électrolyse par la décharge de A_1 assurent à partir de τ_1 une contribution partielle au courant total croissant en ϱ/t .

3. On comprend qu'il est dès lors possible d'étendre le traitement au cas du processus de décharge à plus de deux étapes. En effet, ainsi qu'il l'a été démontré pour

a_3 , les concentrations a_q des particules A_q se déchargeant à la $q^{\text{ième}}$ étape ont, au moment $\tau_1 + \tau_2 \dots + \tau_{q-1}$ choisi comme nouvelle origine des temps, une distribution semblable à a_2 . A cet instant, la répartition de l'ensemble des particules $A_1, A_2 \dots$

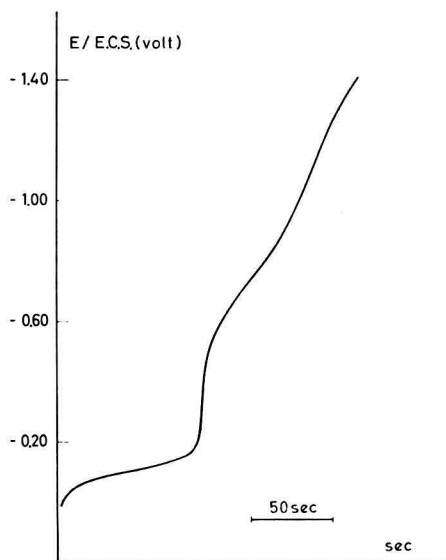


Fig. 3. Réduction de l'oxygène dissous dans NaClO_4 , 0.4 M: $\rho = 3.36 \cdot 10^{-6} \text{ A cm}^{-2} \text{ sec}^{1/2}$.

A_{q-1} peut se mettre sous une forme équivalente à (6), ce qui revient à réunir les $q-1$ étapes en une seule. Soit



Après modification adéquate des conditions initiales et aux limites, on est ramené au traitement du processus en deux étapes. On trouve

$$a_q(0, t) = \frac{\rho}{2(n_1 + n_2 \dots + n_{q-1})F} \sqrt{\frac{\pi}{D_{A_q}}} (\tau_1 + \tau_2 \dots + \tau_{q-1}) - \frac{\rho}{2n_q F} \sqrt{\frac{\pi}{D_{A_q}}} t \quad (54)$$

et au temps de transition τ_q (compté à partir de $\tau_1 + \tau_2 \dots + \tau_{q-1}$)

$$\frac{\tau_1 + \tau_2 \dots + \tau_{q-1}}{n_1 + n_2 \dots + n_{q-1}} = \frac{\tau_q}{n_q} \quad (55)$$

Il résulte finalement de (50) et (55) que

$$\frac{\tau_1}{n_1} = \frac{\tau_2}{n_2} \dots = \frac{\tau_q}{n_q} \quad (56)$$

CONCLUSION

Le caractère additif des temps de transition, et le fait que la morphologie et position des divers paliers est in affectée par l'occurrence des réactions de décharge antérieures, distingue avantagusement la méthode proposée de la chronopotentiométrie à courant constant.

Étant donné que les courbes $E = f(t)$ ont exactement les propriétés des courbes polarographiques $E = f(i)$, on dispose en fait d'une méthode oscillographique donnant l'image fidèle d'un polarogramme classique à l'opposé des méthodes à balayage en tension où l'on observe des ondes en forme de pics étalés, dont l'amplitude est fonction du degré d'irréversibilité de la réaction de décharge et de la vitesse du balayage, et où l'application du principe d'additivité est limitée par l'incertitude sur l'extrapolation des courants-limites partiels.

RÉSUMÉ

Un calcul rigoureux permet de montrer le caractère additif des temps de transition dans la méthode chronopotentiométrique où le courant imposé est de la forme $i = \rho/\bar{i}$. La morphologie des divers paliers des courbes de polarisation pour une valeur donnée de ρ reste également in affectée par les réactions de décharge voisines.

SUMMARY

It is mathematically shown that transition times observed in $i = \rho/\bar{i}$ chronopotentiometry are additive quantities, and that the potential-time curve for a given depolariser and a given value of ρ is independent of the number and length of the previous steps.

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Note ajoutée lors de la correction

Il ressort d'un article récent de W. REINMUTH (*Anal. Chem.*, 32 (1960) 1509) que l'antériorité de conception de la méthode chronopotentiométrique en $i = \rho/\bar{i}$ revient à M. SENDA, par une publication (*Revs. Polarography Japan*, 4 (1956) 89) non répertoriée dans *Chem. Abstr.*, dont l'existence nous était inconnue.

Short Communications

Note on "Reference electrodes and tensions" (J. Electroanal. Chem., 1 (1960) 265)

A careful reading of the paper by MILAZZO AND BOMBARA suggests perhaps a clarification of the following points.

(a) For the benefit of American readers, the cell tension (Zellspannung) $U(\text{cell})$ is defined, following the C.I.T.C.E. conventions¹, as equal to $-E(\text{cell})$, where $E(\text{cell})$ is the I.U.P.A.C. Stockholm cell e.m.f. of 1953², *i.e.*, $E(\text{cell}) = \varphi(\text{right}) - \varphi(\text{left})$, where the φ 's are the inner electrical potentials of the two metallic conducting terminals of the cell, on open circuit.

(b) The first equation on p. 277 is *not* the first derivative of the silver-silver chloride standard electrode tension, as given by BATES AND BOWER³. Instead it is the quantity that, multiplied by t , must be added to the 0° tension to obtain the t° tension. The first derivative, in the mathematical sense, would be given by a similar expression in which the three coefficients are multiplied by 1, 2 and 3 respectively; this would then require integration to go from 0° tension to the t° tension, giving finally the same practical result.

(c) In DE BETHUNE, LICHT AND SWENDEMAN's definition of the thermal temperature coefficient of electrode tension

$$(dU/dT)_{th} = S^*_I/nF,$$

the entropy term S_I^* termed *entropy of electrical transport* is defined as the entropy transported reversibly from the hot to the cold *heat reservoir* by the passage of n faradays of positive electricity through the cell from the cold to the hot electrode, in the limit of a vanishing temperature difference between heat reservoirs, and this is the correct thermodynamical definition. By suitable experimental arrangement, *i.e.* by making each halfcell large enough, it is possible to consider each halfcell as constituting its own heat reservoir in the thermodynamical sense.

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- ¹ C.I.T.C.E. Conventions: P. VAN RYSELBERGHE (Chairman): Reports of Commission No. 2 C.I.T.C.E. *Electrochemical Nomenclature and Definitions*:
 (a) *Proc. 6th Meeting, Poitiers, 1954*, Butterworths, London, 1955, pp. 20-49;
 (b) *Proc. 8th Meeting, Madrid, 1956*, Butterworths, London, 1958, pp. 18-47;
 (c) *Proc. 9th Meeting, Paris, 1957*, Butterworths, London, 1959, pp. 176-219; and report presented to Physical Chemistry Section of I.U.P.A.C. (in the press).
 A large abstract of (c) will be published shortly in *J. Electroanal. Chem.*
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 J. A. CHRISTIANSEN AND M. POURBAIX, *Compt. rend. 17th Conf. I.U.P.A.C., Stockholm, 1953*, pp. 82-84;
 T. S. LICHT AND A. J. DE BETHUNE, *J. Chem. Education*, 34 (1957) 435;
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The redoxokinetic effect - a simple picture

When an alternating current is impressed on an electrode, its mean electrode potential departs from the equilibrium value. This phenomenon was first observed by DOSS AND AGARWAL¹⁻⁴, who described it as the "redoxokinetic effect". The term "faradaic rectification" has also been used by some later workers⁵⁻⁷.

In recent years, the phenomenon has assumed importance. The sensitive electro-analytical technique⁶ of radio-frequency polarography is based on this effect. It has also been utilized to determine kinetic parameters in electrode reactions. The purpose of this brief communication is to present a simple picture of this effect*.

Consider, for convenience of exposition, that the a.c. has a square waveform, and that the galvanostatic technique is adopted with the currents i^- and i^+ (in the cathodic and anodic half-cycles) being equal in magnitude. The current driven through the electrode in each half-cycle polarizes the electrode. If the polarization is *symmetrical* in the half-cycles, *i.e.*, if the magnitude of the overpotential during the cathodic and anodic half-cycles is the same, then the mean electrode potential will remain at the equilibrium value. On the other hand, if the electrodes are polarized to different extents during the cathodic and anodic half-cycles, then the mean electrode potential shifts from the equilibrium value. The shift in mean potential is called the redoxokinetic potential Ψ .

PURE ACTIVATION POLARIZATION

If i^- and i^+ are large enough to make the activation overpotentials

$$|\eta_{a^-}| \text{ and } |\eta_{a^+}| > \frac{0.12}{z} \text{ volts}$$

* This note was presented at the First Seminar in Electrochemistry held at Karaikudi, South India, April, 1960.

then the Tafel case of the rate equation can be used*. We have

$$|\eta_{a^-}| = \frac{RT}{\beta zF} \ln \frac{|i^-|}{i_0}$$

and

$$|\eta_{a^+}| = \frac{RT}{(1-\beta)zF} \ln \frac{|i^+|}{i_0}$$

The redoxokinetic potential is given by the difference between $|\eta_{a^+}|$ and $|\eta_{a^-}|$. Thus

$$\Psi = |\eta_{a^+}| - |\eta_{a^-}| = \frac{RT}{zF} \left(\frac{1}{1-\beta} - \frac{1}{\beta} \right) \ln \frac{|i|}{i_0}$$

because $|i^+| = |i^-| = |i|$, and we see that Ψ depends on β , the symmetry factor. If $\beta = 0.5$, then $\Psi = 0$; and if $\beta \neq 0.5$, $\Psi \neq 0$, in which case the mean potential will depart from the equilibrium value.

Let us write $(\beta - 0.5) = x$. Considering β and x as variables, the domains are: $0 < \beta < 1$ and $-0.5 < x < +0.5$. When β (and therefore x) increases, $|\eta_{a^+}|$ increases and $|\eta_{a^-}|$ decreases for a given i_0 . But when $\beta = 0.5$ and $x = 0$, $\Psi = 0$. Hence as β becomes increasingly different from 0.5, *i.e.*, as x deviates from zero, the magnitude of $\Psi = |\eta_{a^+}| - |\eta_{a^-}|$ can also be seen to increase for a given i_0 .

It may be noted that β , by determining the differences in the slopes of the cathodic and anodic Tafel lines also determines the symmetry of the polarization curve. The term "symmetry factor" is therefore most appropriate. It is known that β decides the symmetry of the energy barrier at the cathode-electrolyte interphase. It also governs the distribution of the electrode potential between the forward and backward reactions. Hence, the development of a redoxokinetic potential implies that the energy barrier is asymmetric and hence that the electrode potential is unequally apportioned between the cathodic and anodic reactions.

PURE CONCENTRATION POLARIZATION

In order to obtain a qualitative picture, we shall use the NERNST "diffusion layer" concept. The limitations and approximate nature of this concept have been discussed elsewhere⁹. We have for $|\eta_{e^+}|$ and $|\eta_{e^-}|$, and for $i_{lim.}$ the following equations:

$$|\eta_{e^+}| = \frac{RT}{zF} \ln \left(1 - \frac{i^+}{i_{lim.}^+} \right)$$

$$|\eta_{e^-}| = \frac{RT}{zF} \ln \left(1 - \frac{i^-}{i_{lim.}^-} \right)$$

and

$$i_{lim.} = \frac{zFD}{\delta} C (x \rightarrow \infty)$$

If $i^+_{lim.} \neq i^-_{lim.}$, *i.e.*, if $D_R C_R (x \rightarrow \infty) / \delta_R \neq D_O C_O (x \rightarrow \infty) / \delta_O$, then $|\eta_{e^+}| \neq |\eta_{e^-}|$ and $\Psi \neq 0$. A redoxokinetic potential will therefore develop if there is any difference in the diffusion coefficients D_O and D_R or in the bulk concentrations $C_O (x \rightarrow \infty)$ and $C_R (x \rightarrow \infty)$ of the oxidant O and reductant R involved in the charge transfer reaction.

* The Tafel case has been considered only for simplicity. Even for $|\eta_{a^-}|$ and $|\eta_{a^+}| < 0.12/z$ volts, Ψ depends on β as has been shown by making use of the full rate equation^{2,7,8}.

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Book Reviews

The Polarographic Method of Analysis, 2nd edn. (reprinted), by OTTO H. MÜLLER, Chemical Education Publications, Easton, Pa., U.S.A., 1959, 209 pages, \$5.00.

This book is very well known to everyone engaged in polarographic work. Originally printed in 1941 and thoroughly revised and augmented in 1951, it has been recently reprinted. The aim of the book is to "present a simple account of polarography in a form that can be used by teachers and students of physical chemistry as well as in an advanced course of analytical chemistry". This purpose is fully realized and anyone who wishes to gain some practice in the field of polarography will find described in an elementary fashion the essential points of the polarographic theory, the construction of apparatus, the fundamentals of qualitative and quantitative analysis and of amperometric titrations. A chapter is also dedicated to the more recent developments up to 1950.

Because of the tremendous advances that have been made in the decade since 1950, this book may seem partially obsolete to the present day polarographer. However, if it is realized that the book is not intended as a reference book but rather as a guide for beginners, it should be appreciated for its clarity of exposition, description and presentation of the experiments.

Besides the lack of information on more modern developments, a few minor imperfections must be pointed out: the author uses the misleading term of polarometry to designate amperometric titrations; no mention is given in this chapter on polarometry of any of the more practical and important applications such as the use of a rotating platinum electrode as the indicator electrode; more discussion on the use of amperometric titrations would also be desirable.

Any beginner in the study of polarography will find this book very attractive, and after reading it the interest of many more people may be directed towards polarography.

A. Liberti

J. Electroanal. Chem., 2 (1961) 344

Flame Photometry, von JOHN A. DEAN, McGraw-Hill Book Company, Inc., New York, Toronto, London, 1960, 354 Seiten.

Das vorliegende Buch verdankt seine Entstehung einer Serie von Vorträgen bei einem Symposium der Louisiana State University, U.S.A., und entspricht dem Bedürfnis, die Flammenphotometrie darzustellen, wie sie in den Vereinigten Staaten gehandhabt wird. Es ist also auf amerikanische Verhältnisse zugeschnitten — soweit man hier von Besonderheiten sprechen kann, die über im Lande erzeugte Apparate und Bezeichnungen wie „lb. per sq. in.“ und „cu. ft.“ hinausgehen. Tatsächlich hat der Autor nach eigener Angabe ca. 2000 Veröffentlichungen aus allen Erdteilen zu Rate gezogen, von denen 780 als von allgemeinerer Bedeutung im Literaturverzeichnis angegeben werden. Es ist klar, dass bei einer so weltweiten Literaturdurchsicht Unstimmigkeiten in den analytischen Daten auftreten, die der Autor in dankenswerter Weise auf gleichen Nenner zu bringen, oder vielmehr auf Verschiedenheiten in der Zerstäuber- und Brennerkonstruktion u.ä. zurückzuführen sucht. Es ist ja noch ein ziemlich weiter Weg, bis wir zu einer mehr oder weniger vollkommenen Erkenntnis der Vorgänge in der Flamme gelangen, und gerade die steigenden Anforderungen an Genauigkeit und Zuverlässigkeit lassen immer mehr erkennen, auf wie viele Faktoren man sowohl bei der Anregung als auch bei der Auswertung Rücksicht zu nehmen hat. Diese theoretischen und apparativen Grundlagen bilden fast die Hälfte des Buches und sind von grossem Wert für die Anwendung auf einzelne Fälle und einzelne Elemente in der zweiten Hälfte, sodass der Analytiker nicht so sehr nach minutiösen Arbeitsvorschriften, sondern mit Verständnis der inneren Mechanismen und Zusammenhänge vorgehen kann, und so auch leichter den Weg findet zu anderen, ähnlichen oder grundverschiedenen, Anwendungsbereichen. Der theoretische Teil setzt nicht zu viel voraus für Anfänger, die sich einarbeiten wollen, ohne jedoch aufzuhören, auch für den Fachmann von Nutzen zu sein.

Die ersten 10 Kapitel befassen sich mit den theoretischen und experimentellen Grundlagen der praktischen Flammenphotometrie, wobei Kapitel 2–5 die wesentlichen Grundlagen bringen: Zerstäubung, Charakteristik der Flammen, Anregung der Spektren der Metalle, der Gebrauch von organischen Lösungsmitteln.

Kapitel 6–9 bieten die allgemeinen Prinzipien für die praktische Durchführung von Flammenanalysen: Das Flammenphotometer, Interferenzen, Auswertungsmethoden, Auswahl der optimalen Arbeitsbedingungen. Kapitel 10 behandelt die Absorptions-Flammenphotometrie, von der man eigentlich gerne mehr zu lesen wünschte, und auch wohl in Zukunft mehr hören wird.

In den Kapiteln 11–20 werden die einzelnen Elemente gründlich durchgenommen, die einer Anregung in der Flamme zugänglich sind: beste Anregungsbedingungen für jedes Element, Charakteristik der Spektren (Linien, Banden, Kontinuum, oft mit Abbildungen), Interferenzen

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(getrennt in rein spektrale und Anregungsinterferenzen), Einflüsse von Begleitelementen und Anionen, Empfindlichkeiten, usw.

Kapitel 21–23 bringen einige wichtige geschlossene Anwendungsgebiete: Klinische Analysen, Böden und Pflanzen, Zemente und Glas. Im Abhang finden sich praktische Tabellen zum Ansetzen von Vorratslösungen, analytische Faktoren u.ä.

Das schon erwähnte ausführliche Literaturverzeichnis ist alphabetisch und nicht nach Sachgebieten angeordnet, alle Hinweise darauf finden sich, sehr zahlreich, im Text.

Der Stil ist knapp, jedoch gut verständlich, sodass eine Fülle von wertvollen Hinweisen auf relativ kleinem Raum zusammengetragen ist. Die Ausstattung des Buches entspricht dem guten Ruf der McGraw-Hill Lehrbücher.

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Flammenphotometrie, von R. HERRMANN UND C. TH. J. ALKEMADE, 2. Auflage, Springer-Verlag, Berlin-Göttingen-Heidelberg, 1960, viii + 395 Seiten, 26 Tafeln.

Als BUNSEN an seinen Freund ROSCOE von einer leichten und einfachen Methode der chemischen Analyse durch Spektralbeobachtungen schrieb, hätte er wohl nicht gedacht, dass diese Methode 100 Jahre später ein so umfangreiches Werk über die Flammenphotometrie zeitigen sollte, das nach 4 Jahren schon ein ganz neubearbeitete zweite Auflage erlebt und das doch eigentlich nur das Wesentliche bringt, auf das zu beschränken die Autoren sich auf jeder Seite des Buches bemühen. Die völlige Überarbeitung und Erweiterung waren nötig, da in den letzten Jahren sehr viele Veröffentlichungen über Grundlagen und Anwendungen aufgetaucht sind und da grosse Fortschritte gemacht wurden in der Weiterentwicklung der chemischen Grundlagenforschung (Einfluss von Störpartnern) und ihre Beziehung zur Praxis.

Die Flammenphotometrie erfreut sich steigender Beliebtheit wegen ihrer (relativen) Einfachheit, Genauigkeit und wegen der (ebenso relativ) geringen Kosten der Apparatur. Die Genauigkeit und Zuverlässigkeit der Methode fällt uns aber nicht so einfach in den Schoß: aus den anfänglich rein experimentellen Verfahren ist eine richtige Wissenschaft geworden, bei der die theoretische Erkenntnis direkten Einfluss hat auf die Messergebnisse. Trotz allem ist man aber noch weit von einer absoluten Methode entfernt!

Ein Grossteil der Theorie ist in die Geräte selbst hineingearbeitet, besonders in den Zerstäuber usw. Doch muss der Analytiker auch diese Dinge verstehen, um sinnvolle Arbeit zu leisten und um die Methoden den Analysegegebenheiten anzupassen. Das vorliegende Lehr- und Handbuch behandelt alle diese Fragen gründlich und in knapper Ausführlichkeit, vom wissenschaftlichen Hintergrund angefangen bis zu Details der Apparatur, soweit dies überhaupt in einem einzigen Werk möglich ist. Die Autoren sind Physiker, bzw. Physico-Chemiker, und sind wohl berufen zu dieser Aufgabe, denn die Flammenphotometrie ist eine wesentlich physikalische Analysenmethode.

Es werden keine Arbeitsvorschriften gegeben, und man wird sich den Gründen, die die Autoren dafür (S. 292) angeben, nicht verschliessen können. Das Buch ist eben nicht für Laboranten geschrieben, sondern vermittelt eine vollständigen Ausbildung in diesem Wissenszweig.

Aus dem Inhalt seien nur die grossen Züge und einige Besonderheiten herausgenommen: Ein Vergleich mit der chemischen Analyse und mit anderen emissions-spektralanalytischen Verfahren gibt sehr wichtige Aufschlüsse über die Vor- und Nachteile der Flammenphotometrie, was man von ihr erwarten kann und wo ihre Grenzen liegen. Dann folgen kurz die Grundlagen über allgemeine Vorgänge in der Flamme und die Strahlung von Atomen und Molekülen in ihr. Ein Grossteil des Buches (120 Seiten) ist den Messmethoden und Apparaten gewidmet, wo zunächst die Einrichtungen für die Unterhaltung der Flamme und das Zuführen der Analysesubstanz dargelegt werden. Ausführlich werden die Filtergeräte, die Flammenspektrophotometrie und -spektrographie besprochen, mit allen Einzelheiten mechanischer, optischer und elektronischer Natur. In letzterem Kapitel könnte man wünschen, dass auch die modernen Photohalbleiter erwähnt würden, die zwar in kommerziellen Geräten noch kaum verwendet, doch Aussicht haben dürften, da sie besonders im IR ergiebig sind und ihre Empfindlichkeit u.U. beträchtlich an die von SEV herankommt, ohne jedoch die hohen Betriebsspannungen zu benötigen.

Aber es ist nicht alles Theorie: Es folgen 40 Seiten Allgemeines zur praktischen Ausführung von Analysen, Eichkurven, Nichtmetalle, indirekte Bestimmungsmethoden usw., und was besonders wertvoll ist, 50 Seiten Fehlererkennung und -beseitigung. Erst dann folgen die verschiedenen Anwendungen (40 Seiten) in allen Gebieten, kurz aber inhaltsreich. Eine ausführliche Tabelle gibt die Nachweisgrenzen der Elemente wieder, eine andere die spezifische Beeinflussung durch Störpartner, die jedoch nur die Möglichkeit und Richtung des Einflusses aufzeigt, während für Einzelheiten und Grösse der Störung in jedem Fall auf die entsprechende Literatur verwiesen

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wird. Die Literatur umfasst über 850 Angaben, vorwiegend aus neuerer Zeit, sogar bis zum Frühjahr 1960. Zwei Tabellen von Flammenlinien und -banden (nach Wellenlängen und nach Elementen) sowie eine Übersicht über die kommerziellen Flammenphotometer bilden den Schluss.

Da die Bedeutung der registrierenden Methode ständig zunimmt, sind im Anhang auf 26 herausklappbaren Tafeln 74 Registrierkurven von allen praktisch vorkommenden Elementen aufgenommen, die eine ungemein wertvolle Ergänzung sind und die aufgewendete Mühe des Verlages beim Druck und Binden vollauf rechtfertigen.

Im Übrigen ist es ein Springer-Buch . . .

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Principles and Practice of Gas Chromatography, by ROBERT L. PECSOK, John Wiley & Sons, Inc., New York, and Chapman & Hall, Ltd., London, 1959, xii + 220 pages, £ 2 14s.

As stated in the preface, this short book of 220 pages is the edited and elaborated outcome of a course of lectures given by the authors of the various chapters, organised by R. L. PECSOK at the University of California in 1959.

Its aim is to treat gas chromatography from a practical point of view and it provides a useful introduction, with a clear description of the problems involved. Newcomers to the field should not be disturbed by the imposing list of symbols which introduces the text and which proves to be very useful indeed, and they may be assured that the treatment of the subject is not as mathematical as may appear from a glance at the first few pages.

The index includes 705 references, well selected and arranged according to their year of publication. It is perhaps a pity that the publishers chose a type of letter whose general effect is reminiscent of offset printing; the book would seem to merit a better production.

M. Lederer

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Chemical Analysis, by H. A. LAITINEN, McGraw-Hill Publishing Co., New York and London, 1960, xiv + 611 pages, \$ 12.50, £4 17s.

Whereas there have been many textbooks of different types devoted to instrumental methods of chemical analysis, relatively less attention has been paid in the last two decades to advanced texts on "wet" or "classical" methods of analysis. The volume reviewed is a good example of such a textbook for the advanced student specializing in analytical chemistry as well as a reference book for the practising analytical chemist. Once again it has been shown that the most fundamental and apparently most simple aspect of any branch of science can be adequately treated only by a leading expert in the field. The aim of the book, *viz.* to show that even in inorganic chemical analysis (in contrast to instrumental analysis) there are still problems of a fundamental nature, the solution of which can bring important contributions not only to the fields of chemical and instrumental analysis but to chemistry as a whole, has undoubtedly been achieved. One important feature which distinguishes the volume reviewed from many textbooks on analytical chemistry is that only principles are discussed. For a detailed description of procedures the reader has to look elsewhere. Numerical problems are included at the end of each chapter.

The acid-base equilibria in aqueous and non-aqueous solutions are dealt with first, together with the principles of titrimetric methods based on these equilibria. Discussion of the solubility of precipitates and of factors influencing the formation of precipitates follows. The discussion of basic conditions for gravimetry is supplemented by treatment of the principles of the separation of a gas from a solid or from a liquid. The principles involved in precipitation and complex forming titrations are described next and these are logically followed by the applications of organic reagents for the precipitation and extraction of metals.

From the point of view of electroanalytical chemistry the clearly written chapters on electrode potentials, electrolytic separations and electroanalysis are of the greatest interest. The delicate question of the signs of electrode potentials is treated according to the convention of I.U.P.A.C. The importance of controlled potential methods in electrolysis is stressed. The principles of oxidation-reduction titrations are illustrated by titration curves. The next chapter deals with oxidation and reduction steps preceding the actual determination. These general parts are followed by a discussion of the possibilities offered by particular titrimetric reagents such as per-

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manganate, cerium(IV), iodine, oxy-halogen compounds, etc. The importance of reaction rates in chemical analysis, which has only recently been considered systematically is treated in the next chapter. Distillation, extraction (including partition chromatography), adsorption-, paper- and ion-exchange chromatography and other applications of ion-exchange are all discussed in one chapter. Finally the statistical methods important in chemical analysis and the important but usually not adequately treated process of sampling are included.

The text is well documented by references to textbooks, reviews and also to numerous original papers. The only minor criticism which can be expressed, according to the present reviewer, is that though a discussion of the reactions of organic compounds might well have been included without greatly increasing the size of the book, only the reactions of inorganic compounds are discussed at any length throughout the book. Problems of organic chemical analysis are touched on only occasionally.

In the present case the well-known phrase that this book should not be missing from the shelf of every analytical (including electroanalytical) chemist is really most appropriate.

P. Zuman

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Polarographische Arbeitsmethoden, von M. VON STACKELBERG, Walter de Gruyter, Berlin, 1960, iv + 478 Seiten, D.M. 38.

In den knappen vier Jahrzehnten, seit HEYROVSKY die Polarographie begründete, wurde dieses Gebiet der Forschung von seiner Schule und den Forschern in der ganzen Welt ausserordentlich reich bearbeitet.

Der vorliegende STACKELBERG zeichnet sich dadurch aus, dass er grundlegend in die Theorie und Methodik der Polarographie einführt und dann zu den Arbeitsmethoden übergeht. Die Gliederung wurde so gemacht, dass erst allgemein das Wichtigste über Apparate und deren Handhabung gesagt wird, dann werden spezielle Vorschriften für Analysen gegeben und zwar in reichem Ausmass sowohl für anorganische, als auch organische Bestandteile.

Es folgt noch ein Kapitel über polarographische Titration, über käufliche Apparate, dem Selbstbau von Apparaten und die Nebengeräte, dann ein Kapitel über die Theorie der Stufen und besondere Fälle wie auch über Störungen. Schliesslich werden 100 Seiten der Literatur, nach Sachgebieten geordnet, gewidmet. Diese Literaturzusammenstellung ist für den Praktiker besonders wertvoll, weil sie in Form von Kurzreferaten gebracht wurde.

Diese "*Polarographische Arbeitsmethoden*" sind dem auf diesem Gebiete arbeitenden sicherlich ein unentbehrlicher Wegweiser in Theorie und Praxis. Das Buch ist gleich wertvoll für den Studierenden wie auch für den ausgebildeten Praktiker.

Hervorzuheben ist die klare Sprache und Formulierung, die nicht wenig dazu beiträgt, dass man das Buch gerne zum Ratgeber nimmt.

Wenn auch das Buch nur ein unveränderter Neudruck aus der Auflage aus dem Jahre 1950 ist, so wird sein Wert dadurch nicht gemindert. Der Umfang beträgt 478 Seiten.

F. Bayer

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The Use of Organic Reagents in Inorganic Analysis, by A. I. BUSEV AND N. G. POLIANSKII, translated from Russian by J. T. GREAVES, Pergamon Press, London, 1960, 76 pages, £ 1 is.

This short booklet of only 76 pages, 16 of which are dedicated to bibliographic quotations, summarizes in a concise manner the use of organic reagents in inorganic analysis. The utilization of organic compounds for analytical purposes in the field of inorganic chemistry is continuously growing because of two principal reasons, *i.e.* the continual search for more sensitive and more specific reagents to extend the possibilities of analytical detection and determination to lower limits, and the need to carry out the determinations in the presence of as many as possible other components of the system. It should be welcomed that a concise summary of such reagents, with their uses, has been put at the disposal of analysts. The brevity of the exposition is partly compensated by the size of the bibliography, so that the original literature can easily be found for every interesting reagent or method. In this respect one objection to this booklet is that about one third of the bibliography quoted is in Russian and cannot easily be found, whilst the

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very abundant literature published on this subject, for instance in *Collection Czechoslov. Chem. Commun.* or in *Helv. Chim. Acta*, is nearly ignored.

But in any case for initial references this booklet can be very useful. It is divided into two sections, the first one dealing in general with the use of organic reagents and the second being a rapid survey of the most important methods of determining metallic elements of the various groups.

G. Milazzo

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Handbook of Chemistry and Physics, 42nd edn., Chemical Rubber Publishing Co., Cleveland, Ohio, 1960, almost 3,500 pages, \$ 12.00 (U.S.A.), \$ 12.50 (outside U.S.A.).

This book, which is exceptionally useful to every chemist, reached in 1960 its 42nd edition and this contains many improvements. Some tables have been completely revised, others only partially. The completely new tables are devoted to the following subjects: sublimation data for organic compounds; standard types of stainless and heat-resisting steels; buffer solutions, operational definition of pH; solutions giving round values of pH at 25°; conversion formulae for solutions having concentrations expressed in various forms; composition of electrolytes for mercury half cells; dissociation constants (very widely developed); various tables on surface tensions; diffusion of metals into metals; diffusion in some Ti-alloys; dissociation pressure of CaCO₃; supplementary list of definitions and formulae; interplanetary orbits; components of atmospheric air; bond lengths between carbon and other elements. This illustrates the care with which each edition is prepared. The general presentation and printing are unchanged.

G. Milazzo

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Tables for Identification of Organic Compounds, Chemical Rubber Publishing Co., Cleveland, Ohio, 1960, 256 pages, \$7.

This book is a supplement to the well known "*Handbook of Chemistry and Physics*". It contains a large quantity of data useful for the identification of more than 4,000 compounds belonging to the main classes of organic substances.

For a given class of compounds, arranged according to increasing boiling points (for liquids) or increasing melting points (for solids), are recorded the melting points of the more important crystalline derivatives, and sometimes some physical constants. The last fact is very important because such physical constants are seldom recorded in tables of this kind.

On the other hand, they are also very useful for compounds that fail to give crystalline derivatives or give them with difficulty. For example, the recorded density and refractive index make the identification of alkyl halides easier; and the specific rotation and R_F values in some common chromatographic solvents allow sugars and amino acids to be easily distinguished.

The accuracy and clearness of this book make it very useful for organic chemists and for everyone who is interested in the identification of organic compounds.

The only criticism which can be made is the absence of tables for some important classes of substances, such as aliphatic hydrocarbons and carboxylic acid esters.

L. Mangoni

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1. Fundamental electrochemistry

804 – The reducing power of mercury. E. F. Speranskaya and M. T. Kozlovsky (S. M. Kitov Kazakh State University, Alma-Ata, U.S.S.R.). *Zhur. Anal. Khim.*, 15 (1960) 534.

The reduction of a number of ions with mercury has been studied in various solutions which shift the tension of anodic oxidation of mercury. It has been shown that permanganate and persulphate ions are reduced by mercury in neutral, alkaline and acid solutions: iron(III) and molybdate ions are reduced in non-acidified and acid solutions. Selenite, tellurite, vanadate, iodate, chromate and copper(II) ions are reduced only in acid solutions, and the reduction is strongly affected not only by the acidity of the solution, but also by the presence of other ions which shift the tension of anodic oxidation of mercury. Values of the oxidation tension of mercury during reduction have been determined. They depend on the kind of depolarizer and on the nature of the ion being reduced. It has been shown that in the process of copper and tellurium cementation with cadmium amalgam, mercury participates in the reduction together with the cadmium. [Ot.So.]

805 – Electromotive force measurements in aqueous solutions at elevated temperatures. II. Thermodynamic properties of hydrochloric acid. R. S. Greerley, W. T. Smith, Jr., M. H. Lietzke and R. W. Stroughton (Chem. Div., Oak Ridge National Laboratory, Oak Ridge, and Dept. of Chem., University of Tennessee, Knoxville, Tenn., U.S.A.). *J. Phys. Chem.*, 64 (1960) 1445.

The mean ionic activity coefficient, relative partial molal heat content, relative partial molal heat capacity, and osmotic coefficient of hydrochloric acid have been calculated from electrical tension data for concentrations from 0.001–1.0 *M* at temperatures from 25 to 200° and in some cases 275°. The expanded Debye–Hückel equation was shown to represent the data as well at 275° as at room temperature. [D.S.Ru.]

806 – The conductance of hexafluoroarsenic acid and its lithium, sodium and potassium salts in water at 25°. Gordon Atkinson and Calvin J. Hallada (Dept. of Chemistry, University of Michigan, Ann Arbor, Mich., U.S.A.). *J. Phys. Chem.*, 64 (1960) 1487.

The conductances of HAsF_6 , LiAsF_6 , NaAsF_6 and KAsF_6 were measured over the concentration range 10^{-4} – 10^{-2} *M*, and the data were analyzed by the extended Fuoss–Onsager theory. Three of the salts have anabatic phoreograms, only KAsF_6 approaching a limiting tangent from the bottom. The solution “*a*” values are higher than the crystallographic values by about 1.5 Å, while the K_{A_0} calculated for KAsF_6 is 1.76. [D.S.Ru.]

807 – The impedance of galvanic cells. I. Theory. J. H. Sluyters (Laboratory of Analytical Chemistry, State University, Utrecht, The Netherlands). *Rec. trav. chim.*, 79 (1960) 1902.

Similarly to the graphical methods used in the field of dielectrics the real part of cell impedance is plotted against the imaginary part Z'' or against the product $\omega Z''$ at different angular frequencies ω . Information can be obtained from the diagrams about the determination of reaction rate constants of redox reactions, double-layer capacities, ohmic resistances and diffusion constants. It is pointed out that the diagrams are distorted due to diffusion polarisation which sets a limit to the accuracy of the determinations.

It is shown that electrode reactions with large reaction rate constants cannot be investigated accurately; to achieve a 1% accuracy the reaction rate constant should be less than 10^{-2} . See also following abstract. [F.Vo.]

808 – The impedance of galvanic cells. II. Experimental verification. J. H. Sluyters and J. J. C. Oomen (Laboratory of Analytical Chemistry, State University, Utrecht, The Netherlands). *Rec. trav. chim.*, 79 (1960) 1101.

The impedance measurements were performed at a constant a.c. current using a cell, consisting of a hanging mercury or amalgam drop and a pool of mercury or amalgam with the same composition as the drop. A reproducibility of about 2.5% was achieved. A description is given of an optical method for determining the surface area of the drop.

From the diagrams obtained the diffusion constant of the Hg_2^{2+} ion in 1 *M* HClO_4 is calculated and a concentration dependence is found. An accuracy of about 4% is claimed.

For the Zn amalgam electrode in 1 *M* NaClO_4 + 10^{-3} *M* HClO_4 the following results are reported: reaction rate constant $k_{sh} = 3.26 \cdot 10^{-3}$ cm/sec \pm 3.6%; transfer coefficient $\alpha = 0.70$; double-layer capacity $C = 1.64 \cdot 10^{-5}$ Farad/cm² \pm 3.7%. See also preceding abstract. [F.Vo.]

809 – The Soret effect in some 0.01 N aqueous electrolytes. P. N. Snowdon and J. C. R. Turner (Dept. of Chem. Eng., Pembroke Street, Cambridge, Great Britain). *Trans. Faraday Soc.*, 56 (1960) 1409.

Many investigations have been carried out on the optical determination of the concentration changes set up by the application of a temperature gradient to a solution. It was found, however, that in very dilute solutions optical methods were not sensitive enough. An improved conductometric method of measuring the Soret coefficient of dilute aqueous solutions of electrolytes is described. Results show close agreement to those expected from a convection-free system. Values of the Soret coefficient and heat of transport are given for 31 uni-univalent and 8 polyvalent electrolytes, all at a concentration of 0.01 gequiv./l and a mean temperature of 25°. The heats of transport for the uni-univalent substances are shown to be closely additive functions of ionic contributions, but this is only roughly the case with the polyvalent salts at this concentration.

[M.K.Hus.]

810 – Steric effects in organic polarography. P. Zuman (Polarographic Institute of the Czechoslovak Academy of Sciences, Prague, Czechoslovakia). *Acta Chim. Acad. Sci. Hung.*, 18 (1959) 141.

The reactivity of organic compounds expressed by their polarographic half-wave tensions is influenced by polar as well by steric effects of the substituents. In certain cases it is possible to separate these effects from each other. Certain examples of steric effects are discussed in detail, such as the steric hindrance of coplanarity, the steric hindrance of solvation, possibilities of distinguishing *cis* and *trans* isomers by polarography and of distinguishing diastereoisomers, and also the assumptions to be drawn from polarographic observations with respect to the conformation of compounds. In each of the groups discussed, the applicability of polarographic methods for solving stereochemical problems is shown by adequate examples.

[E.Juh.]

811 – Conductance and viscosity: the KCl-glycerol-water system at 25°C (in Italian). F. Accascina and S. Petrucci (Centro di Studio per la Chimica Generale, Rome, Italy). *Ricerca sci.*, 29 (1959) 1640. Measurements of KCl conductivity were carried out at 25° in various water-glycerol mixtures. The validity of the Fuoss-Onsager theory has been confirmed over a 1000-fold change in viscosity. Theoretical calculations can be performed using the macroscopic viscosity of the solvent. Both the relaxation term and the hydrodynamic term in the relative conductance Λ/Λ_0 are almost independent of the viscosity. An unusual increase in the Walden product with decreasing dielectric constant was observed.

[Fr.Pan.]

812 – Conductance and viscosity: the KCl-water-ethylene glycol system at 25°C (in Italian). F. Accascina and S. Petrucci (Centro di Studio per la Chimica Generale, Rome, Italy). *Ricerca sci.*, 30 (1960) 808.

The electric conductivity was measured for solutions of KCl in several mixtures of water and ethylene glycol. Application of the Fuoss-Onsager theory enabled the conductivity equation coefficients to be elucidated: 1% deviations from theoretical values were shown. The related coefficients, S/Λ_0 , E/Λ_0 and J/Λ_0 were compared with those obtained in glycerol solutions (see preceding abstract): a 10% deviation corresponds to a 100-fold variation in viscosity. Variations of the Walden product were shown in the light of H-bonds.

[Fr.Pan.]

813 – Conductance and viscosity: tetraethylammonium picrate in water-glycerol and water-ethylene glycol at 25°C (in Italian). F. Accascina and S. Petrucci (Centro di Studio per la Chimica Generale, Rome, Italy). *Ricerca sci.*, 30 (1960) 1164.

The conductance was measured of several mixtures with different viscosities containing large ions such as those existing in tetraethylammonium picrate solutions. The limiting equivalent conductivities and association constants were computed; association increases from $K_A = 2$ to $K_A = 7$ as the dielectric constant decreases, the latter value being reached in pure glycol or glycerol. The same variations of Walden product as those reported in previous papers (see preceding two abstracts) are observed.

[Fr.Pan.]

814 – Überspannung und Kinetik der Tl^{3+}/Tl^+ -Redoxelektrode. K. J. Vetter und G. Thiemke (Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin-Dahlem, Deutschland). *Z. Elektrochem.*, 64 (1960) 805.

In 1 N, 5 N und 15 N Schwefelsäure werden die stationären anodischen und kathodischen Stromdichte-Spannungskurven der Tl^{3+}/Tl^+ -Redoxelektrode in Abhängigkeit von der Tl^+ - und Tl^{3+} -Konzentration gemessen. Dabei tritt vorwiegend Durchtrittsüberspannung auf. Aus dem Verhalten von kathodischer und anodischer Überspannung wird auf das Auftreten von zwei hintereinander ablaufenden Durchtrittsreaktionen geschlossen. Stromdichte und Konzentrationsabhängigkeiten lassen sich durch Zuordnung von unterschiedlichen Austauschstromdichten und Durchtrittsfaktoren zu jeder dieser Einzelreaktion deuten. Aus der Konzentrationsabhängigkeit wird über die elektrochemischen Reaktionsordnungen der Reaktionsmechanismus $Tl^+ \rightarrow Tl^{2+} + e$, $Tl^{2+} \rightarrow Tl^{3+} + e$, abgeleitet. Der Durchtrittswiderstand entspricht der angegebenen zweistufigen Reaktionsfolge.

[Ha.Re.]

815 – Die Anwendung der parabolischen Potentialschwelle auf die Untersuchung der Quanteneffekte in der Elektrochemie. St. G. Christov (Lehrstuhl für Physikalische Chemie und Elektrochemie des Chemisch-Technologischen Instituts, Sofia, Bulgarien). *Z. Elektrochem.*, 64 (1960) 840.

Es wird die Durchlässigkeit einer unsymmetrischen parabolischen Potentialschwelle berechnet, die durch Überlagerung von einem linearen Potential auf einer symmetrischen Parabelschwelle entsteht. Die abgeleiteten Formeln sind geeignet, um die Rolle des Tunneleffekts der Kinetik elektrochemischer Vorgänge zu untersuchen. [Ha.Re.]

816 – The solvation of ammonium ions in sulphuric acid. T. G. Bonner (Royal Holloway College, Englefield Green, Surrey, Great Britain). *J. Chem. Soc.*, (1960) 3493.

The method used is based on the dependence of the rate constant of cyclohydration of 4-*p*-toluidine-pent-3-en-2-one on the ratio $[H_2SO_4]/[HSO_4^-]$. It has been found that the solvation number of the ammonium ion appears to be one up to 3 *M* concentrations of ammonium sulphate. An equation is proposed for the H_0 acidity scale; as required by the theory, the slope of the log of the rate constant against the calculated values of $-H_0$ is almost exactly unity. [L.Gi.]

817 – Molten antimony(III) chloride as a "water-like" ionizing solvent (in German). G. Jander and K. H. Swart (Inorg. Chemistry Institute, Technical University, Berlin-Charlottenburg, Germany). *Z. anorg. u. allgem. Chem.*, 299 (1959) 252.

Molten antimony(III) chloride is a "water-like" ionizing solvent for a considerable number of organic and inorganic compounds, especially for covalent ones. Crystalline solvates may be obtained from organic and inorganic compounds: solvation of these compounds in the solution is thus shown. The specific conductivity of fused $SbCl_3$, in the range of 10^{-6} ohm $^{-1}$ cm $^{-1}$ is increased by the dissolving electrolytes. The proposed self-dissociation



is discussed in relation to acid-base problems. Some compounds similarly to water, increase the $SbCl_2^+$ ions in the solution. The preparations of crystalline addition compounds are described. [Di.Ciò.]

818 – Structure of the double layer and electrode processes. II. Effect of the nature of the electrode and application of the thallium-amalgam electrode. Paul Delahay and Marcos Kleinerman (Coates Chemical Laboratory, Louisiana State University, Baton Rouge, La., U.S.A.). *J. Am. Chem. Soc.*, 82 (1960) 4509.

Der Zusammenhang zwischen Doppelschichtstruktur und Elektrodeneigenschaften wird an der Thalliumamalgamtropfelektrode, in Verbindung mit den Redoxsystemen Bromat und Jodat in alkalischer Lösung, Hexacyanochromat(III) in cyanalkalischer Lösung, Chromat in alkalischer Lösung und Tetracyanocadmium(II) in cyanalkalischer Lösung untersucht. Abweichungen von der Tafelgeraden bei Bromat und Veränderungen der Austauschstromdichte bei Hexacyanochromat(III), können quantitativ dargestellt werden, ebenso das Minimum in der Chromatwelle. Ein Maximum in der Tetracyanocadmium(II)-Welle kann in Übereinstimmung mit Messungen an der Hg-Tropfelektrode ebenfalls als Doppelschichteffekt beschrieben werden. [Ha.Re.]

See also abstracts nos. 960, 978, 987.

2. Apparatus and accessories

819 – Transport processes in liquid alloys. I. A transport cell for liquid alloys. Paul C. Mangelsdorf, Jr. (Institute for the Study of Metals, University of Chicago, Ill., U.S.A.). *J. Chem. Phys.*, 30 (1959) 1170.

This electrolysis cell, using a thin horizontal ribbon-shaped capillary, permits the measurement in a single experiment of the resistivity, the electrolytic mobility, and the diffusion rate in a single sample of liquid alloy. The resistivity is determined by a Rubicon Student Potentiometer and the apparatus permits the estimation of 10 mV potentials to half a microvolt with good reproducibility. The apparatus has been used to study the electrolytic mobility and the diffusion of cadmium in mercury at 25° and 150°. The results are found to agree with existing data.

This cell can be used for studying the Haeffner effect, and by passing small currents for very long periods one may measure the ratio between the electrolytic mobility and the diffusion coefficient in exactly the same way as they did. [G.Mar.]

820 – Simple derivative circuits and their applications in physical chemical measurements (in Hungarian). D. Dobos (Lacquer and Paint Industries Co., Budapest IV, Hungary). *Magyar Kém. Lapja*, 15 (1960) 421.

Es wird über einfache derivierenden Stromkreis-Schaltungen, die sogenannten RCL-, RL-, RC-Derivatoren und über Transformator-Derivatoren kurz zusammenfassend berichtet. Die Anwendungen bei der potentiometrischen Titrationsen sind ebenfalls diskutiert. [Ja.Inc.]

821 – Simple potentiometric and dead-stop measuring instrument with transistors (in Hungarian). I. Kerényi (Dept. of Chem., Inst. of National Public Health, Budapest, Hungary). *Magyar Kém. Lapja*, 15 (1960) 329.

Es wird über einen einfachen und im jeden Laboratorium leicht zusammenstellbaren, billigen Messapparat berichtet. [Ja.Inc.]

822 – Dust structural researches and analyses by means of dielectric constant measurements (in German). F. Oehme (Inst. Entw. chem.-phys. Analysenmeth., Weilheim/Obb., Germany). *Z. Naturforsch.*, 14b (1959) 779.

Dielectric measurements on powdered solids may be carried out by theoretical structural considerations as well as by analytical methods. The measuring technique presents a considerably greater difficulty for liquids. The various dielectric constant measuring methods are examined. The "dust method" and the possibility of its new applications are in particular described. [Di.Ciò.]

823 – A new pH-meter cell assembly. P. Bamford (Imperial Chemical Industries, Akers Research Laboratories, Welwyn, Herts., Great Britain). *Lab. Practice*, 9 (1960) 597.

The paper describes an inexpensive apparatus which simplifies and speeds up the adjustment of the pH of a large number of small aqueous samples to a standard value. The cell is a glass cylinder fitted with a tap at the bottom, and a filling funnel at the side. A short rubber bung carries a glass electrode, a calomel electrode in a KCl reservoir with a sintered glass plug, a thermometer and four glass capillaries for conveying the necessary reagents. In use, the pH-meter is standardized in the normal way, the test solution is then poured in and its pH read; with the shaker running, the appropriate reagent is run in until the desired pH is reached. The shaker is stopped and after the test solution has been run off, the cell is washed in preparation for the next sample. [Di.Ciò.]

824 – A modified tank for paper electrophoresis. D. A. Osborn (Department of Pathology, Institute of Laryngology and Otolaryngology, University of London, Great Britain). *Lab. Practice*, 9 (1960) 595.

The soaking of the strip in buffer prior to the application of the material for analysis has always been a major problem which has not been lessened with the introduction of cellulose acetate membrane. An apparatus is described which provides for the soaking of the strips *in situ* in a pre-saturated atmosphere. It also incorporates a simple method of maintaining tension on the strips, and retains relative cheapness and simplicity of construction within the scope of the average worker. The dry strips, either filter paper or cellulose acetate membrane, can easily be inserted and removed. The rigid glass top forms a stable platform for the jig used in micrometer methods of application. [Di.Ciò.]

825 – Contribution au problème des électrodes de membranes. IIIa. Découverte des membranes polarographiques (en allemand). P. Bersier, J. Bersier et F. Hügli (Technicum Winterthur, Suisse). *Helv. Chim. Acta*, 43 (1960) 478.

L'auteur propose un dispositif qui comprend une électrode à goutte de mercure, recouverte d'une membrane en oxyde d'aluminium, sur laquelle se produisent des phénomènes d'adsorption (d'autres substances telle que l'acétylcellulose pourraient aussi être utilisées, comme membrane car elles présentent d'intéressantes propriétés dans ce domaine).

La tension U_1 varie très peu avec la vitesse de variation du potentiomètre. L'auteur donne les courbes relatives à ces phénomènes. Le temps d'écoulement entre deux mesures joue un rôle qui est illustré par des graphiques. Enfin, l'auteur affirme qu'il est possible au moyen de son dispositif d'étudier les phénomènes de diffusion des électrolytes dans les pores des membranes. [De.Mo.]

826 – Carbon paste electrodes. Application to anodic voltammetry. Carter Olson and Ralph N. Adams (Dept. of Chemistry, University of Kansas, Lawrence, Kansas, U.S.A.). *Anal. Chim. Acta*, 22 (1960) 582.

The use of carbon paste electrodes (carbon or graphite intimately mixed with an organic liquid) as substitutes for noble metal electrodes is described. Pretreatment of electrodes, temperature and variation in paste composition effects are studied. The reproducibility of the carbon paste electrode area is good for freshly prepared electrodes, the error being of the order of 5%. In general, successive polarograms obtained with the same electrode seem to have a short time reproducibility

of about $\pm 2\%$. The method offers several distinct advantages in solid electrode voltammetry and can be applied to routine analysis using standard techniques of anodic voltammetry. [P.Me.]

827 – A simple saturated calomel reference electrode for polarography. A. S. Landry (International Cooperation Administration U.S.O.M., Lima, Peru). *Anal. Chim. Acta*, 22 (1960) 391.

A saturated calomel reference electrode which can be readily assembled is described. This half cell has a low resistance, is easily transportable, and materially increases the efficiency of the H-cell in polarography. [P.Me.]

828 – Improved technique of agar-gel electrophoresis on microscope slides. R. J. Wieme (Laboratory of Clin. Medicine, University of Gent, Belgium). *Clin. Chim. Acta*, 4 (1959) 317.

With the technique described, a good separation (at least 9 fractions are detectable in normal human serum) is obtained, using only micro-amounts ($1-3 \mu\text{l}$) and a short time (25 min with 25–35 mA). The apparatus has Pt electrodes, dipping into buffer-containing vessels, which in turn communicate by means of large holes with two inner vessels filled with agar and buffered with the same buffer; between these two agar blocks a microscope slide covered with a layer of gel on which grooves for the initial deposition of the samples are traced is placed gel downwards in order to realize electrical connection. After electrophoresis has been carried out and the sample dried, staining can be made using C.I. acid black 1 in order to detect the fractions. [Ca.Cas.]

829 – Electrophoresis tank suitable for wide applications. R. Frenzt (Inst. of Biol., Science Faculty, Nancy, France). *Clin. Chim. Acta*, 4 (1959) 340.

Description of a tank which is easily adaptable for all kinds of electrophoresis. [Ca.Cas.]

830 – Coloured substances as an experimental tool in the study of electrophoretic techniques. H. Peeters and P. Vuylsteke (St. Jans Hospital, Bruges, Belgium). *Clin. Chim. Acta*, 4 (1959) 58.

Conditions are described under which electrophoretic techniques using particular dyes can be carried out. [Ca.Cas.]

831 – Rotating sample table for multiple polarographic analyses. J. Luck (Minneapolis-Honeywell Regulator Co., Minneapolis, U.S.A.). *Chemist Analyst*, 48 (1959) 18.

Description of an apparatus, consisting of a rotating table of the type used for collecting fractions, with the samples placed in tubes radially disposed about the center; bubblers, to which nitrogen is supplied by means of rubber tubes, passing by the central shaft around which the table rotates, are inserted into the tubes. The comparison and the dropping Hg electrodes are placed on a separate stand; the rotation of the table brings each tube in turn into the proper position: the bubbler is then removed, the electrodes inserted, and the polarogram recorded. [Ca.Cas.]

832 – Low impedance electronic coulometer. J. B. Hudson and F. E. Dickey (Metallurgy and Ceramics Research Dept., and Electrical Equipment Development Section, General Electric Research Laboratory, Schenectady, New York, U.S.A.). *Rev. Sci. Instr.*, 30 (1959) 1020.

The instrument described possesses the advantages of being able to be read directly, reasonably accurate, and easy to build. It also has an extremely low input impedance (15 ohms) which permits its use with low impedance sources of tension. The precision is 0.003 coulomb/min and the stability is 0.1% of the full scale value. [G.Mar.]

833 – Bridge for measuring the the impedance of metal microelectrodes. R. C. Gesteland and Bradford Howland (Research Laboratory of Electronics, Massachusetts Institute of Technology, Cambridge, Mass., U.S.A.). *Rev. Sci. Instr.*, 30 (1959) 262.

This paper describes a bridge intended to measure the series components of high-impedances at the metal–electrolyte interface. This measurement is a useful technique for studying the kinetic relations of metallic electrode reactions. The bridge described will measure impedances with high accuracy to well above 100 megohms when the series resistance and reactance are of a similar order of magnitude. It is based upon superposition of frequency-independent bridge circuits. [G.Mar.]

834 – pH measurements with a glass electrode withstanding 1500 kg/cm² hydrostatic pressure. A. Disteche (Laboratory of General Biology, University of Liège, Belgium). *Rev. Sci. Instr.*, 30 (1959) 474.

This paper describes the properties of a glass electrode assembly submitted to high pressures during pH determinations at large ocean depths. The electrode assembly consists of a bulb-type Corning 0.15 glass electrode with two silver–silver chloride comparison electrodes. The hydrostatic pressure inside and outside the glass electrode are made to compensate continuously by interposing a silicone fluid MS 200 between the inner and outer aqueous solutions.

pH changes resulting from dissociation constant shifts caused by pressure in the acid and buffer solutions are in good agreement with theoretical values for HCl, acetic acid, carbonic acid and acetate buffer. For the bicarbonate buffer, the observed tension difference at any pressure is only 75% of the expected calculated value. Phosphate buffer and sea water have also been tested.

[G.Mar.]

835 – Simple microvolt potentiometer. A. F. Dunn (Division of Applied Physics, National Research Council, Ottawa, Canada). *Rev. Sci. Instr.*, 30 (1959) 203.

A continuously variable auxiliary source of tension of the order of 10–15 μV is connected in series with the galvanometer of an ordinary potentiometric apparatus. The circuit consists of a Wheatstone bridge, with two batteries acting as the ratio arms. It is possible to change the current flowing through the meter from a positive value through zero to a negative value. Such a source enables the galvanometer to be brought to zero deflection, and the corresponding voltage increment read from a meter in the auxiliary potentiometer.

The present meter has the range of 25–0–25 μA and gives voltage ranges of ± 2.5 , ± 25 and $\pm 250 \mu\text{V}$. A voltage increment accurate to better than $\pm 2\%$ (0.5 μV in 25 μV) may be obtained, without the need for interpolating the galvanometer deflections.

[G.Mar.]

836 – Construction and characteristics of Teflon-covered polarographic electrode for intravascular oxygen determination. John Krog and Kjell Johansen (The University Institute for Experimental Medical Research, Ullevål Hospital, Oslo, Norway). *Rev. Sci. Instr.*, 30 (1959) 108.

This electrode is mounted in a heart catheter making it suitable for intravascular oxygen determination in the large vessel. This electrode assembly has the advantage that all its components are behind the membrane and thus are shielded against fluids having a tendency to contaminate the reacting surface of the electrode. The advantages of the Teflon membrane are its high permeability to oxygen, its resistance to surface adhesion of proteins, its rather high mechanical strength and the fact that it can be heat sterilized without damage.

The electrode described has been used satisfactorily for determination of intravascular oxygen tensions in different parts of the vascular system of dogs.

[G.Mar.]

837 – A triangular scanning variable speed polarographic apparatus with synchronized writing recorder (in Italian). P. Papoff, L. Grifone and G. Zuliani (Polarographic Centre, Padova, Italy). *Ricerca sci.*, 30 (1960) 159.

A triangular scanning polarographic apparatus is briefly described, which is able to supply tensions with a 3–500 mV/sec speed. The plot tension/current is given by the recorder for both the cathodic and anodic sides. Routine and continuous flow analysis up to 10^{-7} moles/l can be performed, as well as measurements of reversibility and kinetic parameters.

[Fr.Pan.]

838 – The coulometric titration of H.R.T. fuel in the high-radiation-level analytical facility. Determination of copper, uranium and nickel. A. D. Horton, L. G. Farrar, B. B. Hobbs and W. D. Shults (Oak Ridge National Laboratory, Oak Ridge, Tenn., U.S.A.). *U.S. Atomic Energy Commission TID-7568*, Pt. 2, (1959) 96.

A coulometric titration cell assembly was designed for remote-controlled analysis of homogeneous reactor fuel. Satisfactory determinations can be performed for uranium, copper and nickel in the presence of one another. Six months use and several hours exposure to high beta- and gamma-radiations do not cause significant damage to the cell parts.

[Fr.Pan.]

839 – Applications of radio-frequency to reactor analysis. R. W. Stelzner (Oak Ridge National Laboratory, Oak Ridge, Tenn., U.S.A.). *U.S. Atomic Energy Commission TID-7568*, Pt. 2, (1959) 11.

The adaptability of a constant-current parallel transmission line oscillator in radio-frequency analysis is briefly summarized. In addition to oxalic acid titrations and complexometry, these oscillators have been utilized for monitoring both high-alkali and high-acid concentrations of flowing aqueous streams.

[Fr.Pan.]

840 – Application of operational amplifiers to controlled-potential and derivative polarography. D. J. Fisher (Oak Ridge National Laboratory, Oak Ridge, Tenn., U.S.A.). *U.S. Atomic Energy Commission TID-7568*, Pt. 2, (1959) 7.

The suitability of electronic operational amplifiers in instrumental analysis, chiefly in polarography, is briefly discussed. The paper is a summary of a more complete work which appeared in *Anal. Chem.*, 31 (1959) 1475.

[Fr.Pan.]

841 – Application of semiconductor devices to potentiometric and coulometric titrations. H. C. Jones (Oak Ridge National Laboratory, Oak Ridge, Tenn., U.S.A.). *U.S. Atomic Energy Commission TID-7568*, Pt. 2, (1959) 3.

Silicon diodes as rectifiers and Zener diodes as constant-tension sources can be used to replace the batteries in controlled-tension coulometers and similar apparatus; silicon diodes are also useful as meter protectors. Some transistorized circuits are described which appear to give a high performance with respect to the vacuum tube circuits. [Fr.Pan.]

842 – The performance of measuring devices for dielectric constants (in German). K. Slevogt (Inst. Entw. chem.-phys. Analysenmeth., Weilheim/Obb., Germany). *Mitt. Inst. Entw. chem.-phys. Analysenmeth.*, 3 (1960) 68.

Diskussion der Leistungsfähigkeit von dielektrischen Messgeräten ("Dekametern"). Diese Geräte bestehen so gut wie immer aus einem Präzisionsmessgerät zur Kapazitätsmessung und einer Kondensator-Messzelle. Es erscheint zweckmässig, das Dekameter selbst durch die Messempfindlichkeit $\Delta C/C$, als kleinste noch sicher messbare Kapazitätsänderung ΔC bei der vorliegenden Kapazität C zu definieren. Nach Anschluss der Kondensatormesszelle zur Messung von Dielektrizitätskonstanten ϵ wird als Messempfindlichkeit sinngemäss der Quotient $\Delta\epsilon/\epsilon$ angegeben.

Gegenüber der Messempfindlichkeit ist noch die Ablesegenauigkeit von Bedeutung, welche hauptsächlich durch den mechanischen Aufbau (Skalenteilung, Hilfsmittel zur Ablesung usw.) bestimmt wird. Sie soll im allgemeinen 3–5 mal grösser als die Messempfindlichkeit sein.

Die Messrichtigkeit schliesslich bezeichnet die relative Genauigkeit, mit welcher die Dielektrizitätskonstante unter Bezug auf Standardflüssigkeiten gemessen werden kann. Die Messrichtigkeit wird in der Regel 3–5 mal kleiner als die Messempfindlichkeit sein. [Fr.Oe.]

843 – Simple non-gassing electrode for use in electrophoresis. R. Neihof and S. Schuldiner (U.S. Naval Research Lab., Washington 25, D.C., U.S.A.). *Nature*, 185 (1960) 526.

Palladium was found to dissolve considerable amounts of hydrogen when used as a cathode in an electrolytic cell, PdH_x being formed. So long as its formation is faster than the combination reaction of atomic hydrogen on the electrode surface, no molecular hydrogen will be evolved until the solubility of hydrogen in palladium is exceeded, a condition which is manifested in closed electrophoresis systems. At the anode, oxygen or other gases will not be evolved and the current density is not excessive. A palladium anode weighing 1 g, if precharged to a hydrogen/palladium atomic ratio of 0.5, can deliver a current of 10 mA for more than 12 h before the hydrogen is exhausted. [M.K.Hus.]

844 – Regeneration of cellulose acetate membrane used for zone electrophoresis. S. Jacobs (National Institute for Medical Research, The Ridgeway, Mill Hill, London, Great Britain). *Nature*, 183 (1959) 1326.

The technique of analysing serum proteins by zone electrophoresis involves the use of strips of cellulose acetate membrane which are rather expensive. A method is given for regenerating these strips after use so that it is quite possible to use the membrane several times. The method of regeneration involves placing the used strips in a shallow dish containing 200 ml buffer at pH 8.6 to which 2–4 ml trypsin have been added. The proteins present in quantities of 100–200 μg are completely digested within 2 h at 37–39°, but a protein quantity of 700 μg requires sometimes a period of 16 h. Cellulose acetate is quite stable under the regeneration conditions. [M.K.Hus.]

845 – A reversible nitrate electrode. P. H. T. Beckett (Soil Science Lab., Dept. of Agriculture, Oxford, Great Britain). *Nature*, 186 (1960) 879.

A number of electrodes capable of displaying reproducible nitrate functions have been constructed. These electrodes make the determination of nitrates by potentiometric methods possible. The electrodes are made from slightly lumpy samples of powdered zinc fluoride made into a viscous paste with "Diakon" plastic dissolved in chloroform and coated onto a zinc rod in such a way that several fragments of the salt are in contact with the zinc core and also with the surrounding solution. The electrodes are then aged by standing in 0.4 M calcium nitrate solution for 1–7 days. [M.K.Hus.]

846 – Automatic recording velocity-servo potentiometric titrator. M. T. Kelley, D. J. Fischer and E. B. Wagner (Anal. Chem. and Health Physics Div., Oak Ridge National Laboratory, Oak Ridge, Tenn., U.S.A.). *Anal. Chem.*, 32 (1960) 61.

The titrator utilizes an improved, transistorized intermittent balance circuit, a slow pen balanced servo-motor in the recorder and a "Thinking" velocity servo-mechanism to control the rate of addition of the titrant automatically, continuously and proportionately. Over-titration caused by mixing delay is avoided. Complete electronic drawings and construction details are given. Test titration is carried out with uranium and 0.1 N ferric sulfate. The true shape of the potentiometric curve is drawn by the pen recorder. [Kl.Gr.]

847 – Use of an unbalanced bridge circuit in high-frequency titrimetry. J. M. Walker, J. L. Lambert

and L. D. Ellsworth. (Dept. of Physical Science, Kansas State College, Pittsburg, Kan., U.S.A.). *Anal. Chem.*, 32 (1960) 9.

The feasibility of using a modulated off-balance radio-frequency signal originating from the detector side of a high frequency impedance bridge as a method for performing high frequency titrations is investigated. An equation is derived relating the unbalance of the bridge as measured by a voltmeter to that of the true admittance obtained under balanced conditions. A new titration cell with a magnetic stirrer is used. A General Radio Type 1001-A standard signal generator and a Type 821-A Twin T impedance bridge are used with a National Communications receiver Model NC-98 to amplify the modulated signal from the bridge. The advantage of this method is that the titration data are obtained in the form of voltmeter readings. A block diagram of the apparatus and several titration curves are given. [Kl.Gr.]

848 – Détecteur électrolytique de vapeurs et de gaz dans l'atmosphère. A. Berton. *Bull. soc. chim. France*, (1959) 536.

L'auteur propose la construction d'une pile très simple pouvant jouer le rôle de détecteur de gaz. Cette pile est constituée par une boucle de fil de cuivre retenant par capillarité une gouttelette de liquide réactif: la seconde électrode centrale est en plomb. Ces deux électrodes sont courtcircuitées sur un galvanomètre. On note le passage d'un courant électrique plus ou moins intense en présence de certains gaz ou vapeurs. [Bad.Lam.]

849 – The use of fixed mercury electrodes in oscillographic polarography (in Russian). Ya. P. Gokhstein (Institute of Geochemistry and Anal. Chemistry, Academy of Science, U.S.S.R.). *Zhur. Anal. Khim.*, 15 (1960) 541.

A review article, dealing with the use of fixed electrodes in oscillographic polarography. Principles, apparatus and methods are explained. The author sees the main use of this method in the automatic control of industrial solutions, since it has the advantages of high sensitivity, selectivity and reproducibility of results. [Ot.So.]

850 – Automatic evaluation of polarography with a vibrating Pt electrode (in Russian). V. M. Leontiev and N. A. Fedotov (L. J. Karpov Physico-Chemical Research Institute, U.S.S.R.). *Zavodskaya Lab.*, 26 (1960) 276.

A vibrating Pt electrode was used with a vibration frequency of 50 Hz and 1 mm amplitude. The authors publish a diagram of the polarographic circuit for the automatic registration of polarisation curves in high-resistance vessels. The polarisation current, as well as the tension of the indicating electrode against the comparison electrode, are measured by a type EPPO9 potentiometer. The authors give polarisation curves of voltage-polarisation current for the reduction of Fe^{3+} in 0.5 N HCl. The current intensity is proportional to concentration and depends on the vibration of the electrode. It may be increased to 3.5 times the value obtained with a stationary electrode. [Ot.So.]

851 – Oscillopolarography with an amalgamated Ag electrode. E. M. Skobetz and V. I. Shapiro (Ukrainian Academy of Agricultural Sciences, U.S.S.R.). *Zavodskaya Lab.*, 26 (1960) 278.

The authors describe a polarographic circuit which gives better results when used with an amalgamated Ag electrodes than have been obtained previously. [Ot.So.]

852 – Building a high-frequency titrator for instructional use. J. K. Clinkscales, Jr. and Herschel Frye (College of the Pacific, Stockton 4, Calif., U.S.A.). *J. Chem. Educ.*, 37 (1960) 304.

Instructions and circuits are given for the construction of an inexpensive high-frequency titrator suitable for college instruction in instrumental analysis. The unit has a range of 120 megacycles and is balanced with the aid of earphones. [D.S.Ru.]

853 – Determinations of reaction rates with an a.c. conductivity bridge. A student experiment. John P. Chesick and A. Patterson, Jr. (Yale University, New Haven, Conn., U.S.A.). *J. Chem. Educ.*, 37 (1960) 242.

The solvolysis of tertiary butyl chloride is studied by means of conductivity measurements. The circuit and instructions for assembling it are given. [D.S.Ru.]

854 – A semiautomatic polarograph: a low cost instrument for student use. G. Wilson Drake and C. B. Johnston (University of Houston, Texas, U.S.A.). *J. Chem. Educ.*, 37 (1960) 240.

Instructions are given for assembling a synchronized slide-wire and paper drive to facilitate the current plot. [D.S.Ru.]

855 – Electrolytic isolation of non-ferrous inclusions in steel with the use of a modified Klinger and Koch apparatus. L. Brháček, J. Janáček and A. Šmrhová (Research Inst. VŽKG, Ostrava, Czechoslovakia). *Hutnické listy*, 14 (1959) 54.

Using the apparatus described (for details see text), with a high current density (0.1 A/cm²) and a suitable anolyte (Na-citrate: citric acid : KBr : NaCl : KI = 40 : 10.5 : 15 : 20 : 1 g in 1 l H₂O) and catholyte (add 1 ml of 1 N Na₂CO₃ to 86 g of citric acid, and make up to 1 l with H₂O), a shorter time for the isolation is required than in the apparatus described by Klinger and Koch (*Arch. Eisenhüttenw.*, 11 (1938) 569. [Ca.Cas.]

856 – Zone-sharpening in paper electrophoresis. A method allowing application of dilute protein solutions. S. Hjerten (Uppsala University, Sweden). *Biochim. Biophys. Acta*, 32 (1959) 531.

Place a cellophane dialysis tube (5 cm diameter) filled with the buffer under the paper sheet, parallel to and a few cm from the line of application of a large sample of the solution (0.1–0.2 ml), and start electrophoresis; after a suitable time has elapsed all the proteins will be trapped in a narrow zone on the tube line where a sharp fall of the potential gradient occurs: after the tube has been removed electrophoresis is resumed in the usual way. [Ca.Cas.]

857 – Electronic controlled-potential coulometric titrator for plutonium analysis. M. T. Kelley, H. C. Jones and D. J. Fisher (Oak Ridge National Laboratory, Oak Ridge, Tenn., U.S.A.). *Talanta*, 6 (1960) 185.

An instrument which performs coulometric redox titrations at a controlled-tension is described. A chopper-stabilized printed-circuit operational difference amplifier combined with a transistor current amplifier is used to control the tension of the electrode at which the desired reaction takes place. A portion of the electrolysis current is integrated by a stabilized printed-circuit operational amplifier connected as a time-integrator, the integral being read as a tension. The instrument is operated completely from an a.c. line and can be operated with either manual or automatic cut-off. Accurate coulometric titration of small amounts of substances with high equivalent weights is possible because of the high stability of the integrator. A method for the determination of plutonium with this titrator has been developed. [Ja.Inc.]

858 – Some applications of high-frequency titrimetry. D. L. Manning and O. Menis (Oak Ridge National Laboratory, Oak Ridge, Tenn., U.S.A.). *Talanta*, 6 (1960) 30.

A parallel transmission line oscillator operating at 190 Mc/s was demonstrated to be a useful instrument for high-frequency titrations. The end-point is established by graphically recording either the oscillator grid current or the *IR* drop, which is produced by passing this current through a load resistor, *versus* the volume of titrant and extrapolating the two segments of the titration graph to a point of intersection. The delivery of titrant at a constant rate is accomplished through the use of a 900-S single-speed infusion-withdrawal pump, equipped with a 2 rev/min synchronous motor. This device delivers 1.304 ± 0.004 ml of titrant/min. For some of the titrations, however, an alternate motor-driven burette can be used.

The instrument was utilised for the titrations of strong acid, free acid in the presence of uranium, sulphate with barium chloride and of thorium with oxalic acid as well as with EDTA. The effect of uranium, of aluminium, of iron(II) and of acetate on the titration of thorium with EDTA was investigated. It is finally concluded that the parallel transmission line oscillator is a useful instrument for following chemical changes in rather complex solutions. [Ja.Inc.]

See also abstracts nos. 808, 820, 951, 980, 990, 1004.

3. Polarography

859 – Polarographic determination of lead and antimony impurities in tin metal (in Hungarian). J. Kádár-Pauncz (Inst. of National Feeding and Nutrition Sciences, Budapest, Hungary). *Magyar Kém. Lapja*, 15 (1960) 330.

Die Zinnprobe wird in Salzsäure, in Anwesenheit von KClO₃ gelöst, und nach Reduktion mit Sulfid werden die als Verunreinigung vorhandene Blei- und Antimonionen in KCN-haltiger, alkalischer Lösung polarographiert. Kupfer und Arsen stören die Methode nicht.

Arbeitsvorschrift: 0.1 g der Probe versetzt man mit 5 ml 10%-iger Weinsäure-Lösung, nach Eindampfen mit 5 ml 20%-iger HCl-Lösung und nach und nach, am Wasserbad, mit insgesamt 0.6 g festem KClO₃. Nach erneutem Eindampfen der Lösung nimmt man den Rückstand mit 4 ml konz. HCl auf und erwärmt nach Zugabe von 1 g festem Na₂SO₃ unter Rückflusskühler eine halbe Stunde. Nach Beendigung der Reduktion dampft man wieder ein, überspült mit 20%-iger NaOH-Lösung in einen 50 ml Messkolben und füllt nach Zugabe von 5 ml 10%-iger KCN-Lösung mit 20%-iger

NaOH-Lösung bis Marke auf. Den Sauerstoff vertreibt man mit Stickstoff und polarographiert unmittelbar.

Die Bestimmung des Kupfers ist nach Auflösung der Probe und nach Zugabe der Weinsäure-Lösung in $N \text{ NH}_4\text{OH-NH}_4\text{Cl}$ Grundlösung ausführbar. [Ja.Inc.]

860 – Amperometric determination of cobalt in ferrous and non-ferrous metals by potassium ferricyanide (in Hungarian). I. Bozsai (Csepel Iron and Metal Works, Budapest, Hungary). *Magyar Kém. Lapja*, 15 (1960) 423.

Die Methode beruht auf der Oxydationsreaktion des Cobalt(II)-ions mit Kaliumhexacyanoferrat-(III) in ammoniumtartrathaltigem Medium. Der Endpunkt der Reaktion wurde durch die an einer drehenden Mikroplatinelektrode entstehenden Stromintensitätsveränderung bestimmt.

Arbeitsvorschrift: Man löst die Stahl-, Silumin-, Aluminium-, Nickel (u.s.w.) Probe in Schwefel- bzw. Salzsäure, oxydiert mit Salpetersäure, spült die Lösung in einen Messkolben und füllt bis Marke auf. Bei Stahl- und Siluminproben neutralisiert man vorher mit ZnO um die störenden Metal (Eisen u.s.w.) Ionen zu fällen. Nach der Filtrierung pipettiert man 50 ml in eine Grundlösung, die aus 10 ml 30%-iger Weinsäure-, 70 ml Ammoniumhydroxyd-Lösung (Dichte 0.91) und 5 ml Hexacyanoferrat(III) Masslösung besteht. In Anwesenheit von Kalomel und drehender Platin-Elektrode bei 0.00 V Spannung titriert man die überflüssige Hexacyanoferrat(III)-Ionen mit Hilfe einer Mikrobürette, mit CoCl_2 -Masslösung zurück. Die Hexacyanoferrat(III) Masslösung enthielt je liter 11.000 g $\text{K}_3\text{Fe/CN}_6$, während die CoCl_2 -Masslösung 2.000 g Co. [Ja.Inc.]

861 – Polarography of thiocyanate ion. Complex ion formation with mercury(II) ion. C. J. Nyman and G. S. Alberts (Dept. of Chem., Washington State University, Pullman, Wash., U.S.A.). *Anal. Chem.*, 32 (1960) 207.

The polarographic behavior of thiocyanate ion-containing solutions is investigated. The tension-concentration data for the anodic oxidation of mercury in solutions of thiocyanate can be interpreted by the formation of complex ions of the type $(\text{Hg}(\text{SCN})_j)^{(2-j)}$, where j has the values 2-4. The formation constants of the complexes are $k_2 = 1.18 \cdot 10^{16}$, $k_3 = 8.9 \cdot 10^{18}$ and $k_4 = 8.7 \cdot 10^{20}$. [Kl.Gr.]

862 – The application of the cathode ray polarograph in food analysis. J. S. Hetman (Southern Analytical Ltd., Camberley, Surrey, Great Britain). *Lab. Practice*, 9 (1960) 563.

The work describes polarographic methods for the simultaneous determination of Cu, Pb and Zn in various foods and drinks. A new technique has been developed which enables these determinations to be carried out in 1-2 h. A cathode ray polarograph is used for the estimation of each metal. The high sensitivity and resolution of the instrument eliminates the necessity of preliminary chemical separation. The estimation of copper and zinc in beer, simultaneous determination of copper, lead and zinc in meat extract, copper, lead and zinc in wine, and vitamin C, saccharin, sulphur dioxide and benzoic acid in soft drinks, is also described. [Di.Ciò.]

863 – Post adsorption wave of cuprous thiocyanate in polarograms of dilute thiocyanate solutions containing copper(II). I. M. Kolthoff and Y. Okinaka (School of Chemistry, University of Minnesota, Minneapolis, U.S.A.). *J. Am. Chem. Soc.*, 82 (1960) 3528.

In verdünnten Thiocyanatlösungen werden bei der polarographischen Reduktion von Cu(II) -Thiocyanat an der Hg-Tropfelektrode drei polarographische Wellen erhalten. Aus der Abhängigkeit der Wellenhöhe von der Kupferkonzentration und der Tropfenfallhöhe wird die dritte Welle der Reduktion einer adsorbierten monomolekularen Kupferthiocyanatschicht zugeordnet. Die Annahme wird durch die Gestalt der Elektrokapillarkurve, und der Änderung der Halbwellenspannung mit der Kupfer- und Thiocyanatkonzentration, sowie durch Messungen an einer rotierenden Hg-Tropfelektrode bestätigt. [Ha.Re.]

864 – Solvent effects on the polarographic reduction of metal ions. II. Nitrile solvents. Robert C. Larson and Reynold T. Iwamoto (Dept. of Chemistry, University of Kansas, Lawrence, Kan., U.S.A.). *J. Am. Chem. Soc.*, 82 (1960) 3526.

Es wird die polarographische Reduktion von Metallionen in Benzonitril, Phenylacetonitril, Acrylnitril, Propionitril und Acetonitril untersucht. Dabei wird eine zunehmende Erschwerung der Reduzierbarkeit in der angeführten Reihenfolge beobachtet. Ein Reaktionsmechanismus, der die Lösungsmittelmoleküle in den Reduktionsverlauf mit einbezieht, wird angegeben. Es wird vermutet, dass die Reduktion der Metallionen nach diesem Mechanismus durch die Gegenwart einer konjugierten Doppelbindung mit erleichtertem Elektronenaustausch im Lösungsmittelmoleküle, stark gefördert wird. Die Wirksamkeit des Phenylacetonitrils wird dagegen dessen niedriger Dielektrizitätskonstante (18.7) zugeschrieben. Die Halbwellenspannungen der untersuchten Redoxsysteme in den angeführten Lösungsmitteln sind tabelliert. [Ha. Re.]

865 – Solvent effects on the polarographic reduction of metal ions. I. Benzonitrile–acetonitrile. Robert C. Larson and Reynold T. Iwamoto (Dept. of Chemistry, University of Kansas, Lawrence, Kan., U.S.A.). *J. Am. Chem. Soc.*, 82 (1960) 3239.

In Benzonitril und Acetonitril als Lösungsmittel wurde die polarographische Reduktion einer Reihe von 1-, 2- und 3-wertigen Metallionen untersucht. Ein Vergleich der gewonnenen Halbwellenspannungen mit Infrarotuntersuchungen in den gleichen Lösungsmitteln lässt auf einen besonderen Reduktionsmechanismus schließen, in dem die Lösungsmittelmoleküle komplexe Zwischenverbindungen mit den Kationen eingehen, die dann ihrerseits der Reduktion unterliegen, wobei die Wirkung des Benzonitrils stärker hervortritt, als die des Acetonitrils. Nebeneffekte, die durch die Gegenwart geringer Mengen Wassers und Sauerstoffs hervorgerufen sind, werden diskutiert. Die Halbwellenspannungen der untersuchten Reduktionssysteme sind tabelliert.

[Ha.Re.]

866 – Effect of polycyclic aromatic hydrocarbons on the polarographic maximum of copper. C. E. Searle (Cancer Research Laboratories, Dept. of Pathology, The Medical School, Birmingham, Great Britain). *Nature*, 184 (1959) 1716.

A pronounced maximum occurs in the polarograms of cupric sulphate and sulphuric acid in methanol. It was reported that this maximum is suppressed by some carcinogenic hydrocarbons, an effect which is now accepted as an established property of these hydrocarbons. This study deals with a large range of hydrocarbons in order to elucidate whether or not there is any correlation between carcinogenicity and suppression of the copper maximum. In this respect, polarograms were taken with a Cambridge Heyrovsky-type polarograph.

It was generally found that whenever the number of the aromatic rings in the hydrocarbon was increased, the polarographic maximum of the copper became smaller. In certain cases there was very little difference between the effects of the non-carcinogenic and the highly carcinogenic isomer.

[M.K.Hus.]

867 – Microdosages polarographique, spectrophotométrique et par activation aux neutrons, du cobalt dans une fonte. Etude comparative. J. Vogel, D. Monnier et W. Haerdi (Laboratoires de chimie minérale, de chimie analytique et de microchimie, Université de Genève, Suisse). *Helv. Chim. Acta*, 43 (1960) 1254.

Les auteurs proposent une méthode de dosage du cobalt au polarographe à rayons cathodiques sur des échantillons de fonte. La prise initiale est de 5 mg, les séparations se font au moyen d'une résine "échangeur d'ions" et par extraction à la dithizone. Les erreurs sont de 6% environ. Le contrôle des pertes se fait par marquage au cobalt-60. Les résultats obtenus sont comparés à ceux donnés par la spectrophotométrie et par la méthode d'activation aux neutrons. Cette dernière est la plus simple, la méthode spectrophotométrique la plus sensible et la plus précise, et la méthode polarographique la plus rapide.

[De.Mo.]

868 – Quantitative determination of methyl 1-methylbutylidene cyanoacetate by a polarographic method (in Polish). H. Marciszewski (Anal. Laboratory, Pharmaceutical Institute, Warsaw, Poland). *Chem. Analityczna*, 5 (1960) 119.

A polarographic method for the determination of the methyl ester of 1-methylbutylidene cyanoacetic acid has been developed. This method could be successfully used for the determination of this compound during its reduction to the ester of 1-methylbutyl cyanoacetic acid. The calibration curve was linear over the concentration range 20–100 $\mu\text{g/ml}$. The substance was dissolved in methanol and diluted 25 times with 0.1 N KCl used as the supporting electrolyte. The half-wave tension $U_{\frac{1}{2}} = -1.72 \text{ V vs. S.C.E.}$ This method enabled the determination of less than 1% of the methyl ester of 1-methylbutylidene cyanoacetate in methylbutyl cyanoacetic acid. Results were compared with those obtained by refractive index measurements.

[Ad.Hu.]

869 – Application of amperometry in kinetic methods of quantitative analysis. I. Catalytic determination of small amounts of molybdenum (in Polish). W. Jedrzejewski (Dept. of Inorganic Chemistry, University of Łódź, Poland). *Chem. Analityczna*, 5 (1960) 207.

Amperometry with two polarized platinum electrodes was used for the determination of the concentration of iodine, produced during the H_2O_2 –KI reaction and catalyzed by Mo(VI). The slope of the current–time curve was proportional to the concentration of molybdenum with constant conditions, i.e. H_2O_2 , KI and H_2SO_4 concentrations, and mixing velocity. On this basis Mo was determined over the range $2.96 \cdot 10^{-10}$ – $1.48 \cdot 10^{-9} \text{ M}$, which corresponds to 0.28 – $1.42 \cdot 10^{-7} \text{ g Mo/ml}$. The error in the determination was less than $\pm 6\%$. The current–time curves were recorded automatically by means of a Radiometer PO 3k polarograph with 50 mV voltage applied to the two platinum indicator electrodes.

[Ad.Hu.]

870 – Ion exchange properties of papers for cadmium and indium separation (in Polish). W. Kemala

and K. Brajter (Dept. of Inorganic Chemistry, University of Warsaw, Poland). *Chem. Analityczna*, 5 (1960) 219.

A polarographic method was used for recording the eluate composition of an In^{3+} and Cd^{2+} mixture separated on Whatman No. 4 chromatographic paper, using frontal analysis. $0.2\text{ N NH}_4\text{Cl}$ was used as the supporting electrolyte and the pH of the solution was changed over the range 2.5–4.2. Adsorption and therefore ion separation was influenced by the pH and the supporting electrolyte concentration. [Ad.Hu.]

871 – Determination of small amounts of iron, manganese and copper in nickel (in Polish). W. Kemula, K. Brajter, S. Cieřlik and H. Lipińska-Kostrowicka (Dept. of Inorganic Chemistry, University of Warsaw, Poland). *Chem. Analityczna*, 5 (1960) 229.

A method for iron, copper and manganese determination in nickel has been developed. Copper was directly determined in an HNO_3 solution of the sample, using $\text{NH}_3\text{--NH}_4\text{Cl}$ supporting electrolyte. Iron and manganese were precipitated as hydroxides on Lewatite MII anion exchanger, previously washed with ammonia. Nickel and other cations (Co, Cu, Zn) were detected in the eluate as ammonia complexes. Iron and manganese were eluated with sulphuric acid, and their content was determined colorimetrically with thiocyanate and as permanganate, respectively. Nickel containing the following impurities was analysed: 0.5–1% Cu, 0.03–0.1% Fe, 0.03–0.1% Mn. Precision was about 3%. [Ad.Hu.]

872 – Catalytic determination of microgram amounts of copper by amperometric measurements (in Polish). K. Czarnecki (Dept. of Inorganic Chemistry, University of Łódź, Poland). *Chem. Analityczna*, 5 (1960) 377.

Amperometry with two polarized platinum electrodes has been used for the determination of the ferric iron content during the $\text{Fe}^{3+}\text{--S}_2\text{O}_8^{2-}$ reaction catalyzed by cupric ions. The rate of the reaction depended on the concentration of cupric ions when the other parameters were kept constant. Samples with known and unknown cupric ion concentrations were analysed under identical conditions and for the unknown samples the precision was about $\pm 2\%$. As a calibration curve the relation between the half-life period of the reaction and the copper concentration could be used. The determination was performed in the concentration range 6–30 μg of copper in 10^{-6} M solution. [Ad.Hu.]

873 – Polarographic determination of styrene in polystyrene (in Polish). J. Pařciak (Research Laboratory, Chemical Works, Ořwiecim, Poland). *Chem. Analityczna*, 5 (1960) 477.

Two methods of styrene determination in polystyrene were reinvestigated. They are based on the preparation of a 20% solution of polystyrene in benzene and extraction either with 0.1 M $(\text{C}_4\text{H}_9)_4\text{NI}$ in 75% ethanol or with 75% ethanol. In the latter case, after extraction and phase separation by centrifuging, 0.1 M $(\text{C}_4\text{H}_9)_4\text{NI}$ in 75% ethanol was added to the alcoholic phase in the polarographic cell. It was found that the polarographic wave-height-concentration relationship did not become linear until the styrene concentration was higher than 1.60%. Calibration curves were obtained for deaerated and oxygen-containing solutions. This method makes the determination of 0.1% styrene in polystyrene possible with an error of about 4%.

A new method was developed, in which 0.10 M $(\text{C}_4\text{H}_9)_4\text{NI}$ in dimethylformamide was used as the supporting electrolyte. A benzene solution of polystyrene was added to this solution and after deaeration the solution was analysed polarographically. The half-wave tension $U_{\frac{1}{2}} = -2.46\text{ V}$ vs. S.C.E. The calibration curve was strictly linear and the determination shorter and more convenient. By this method 0.03% styrene in polystyrene could be determined with an error of about 1.5%. [Ad.Hu.]

874 – Polarographic determination of 1,3-dimethyl-4-amino-5-nitrozouracyl (in Polish). H. Marciszewski and A. Greszkiewicz (Anal. Laboratory, Pharmaceutical Institute, Warsaw, Poland). *Chem. Analityczna*, 5 (1960) 509.

The method of 1,3-dimethyl-4-amino-5-nitrozouracyl determination (O. Manouřek, M. Konupćik and J. Davidek, *Českoslov. Farm.*, 6 (1957) 593) was modified by using 15 ml of 0.1 $\text{N NH}_4\text{OH}$ for dissolving 100 mg of the sample. This solution was diluted 50 times with Britton-Robinson buffer of pH 6. The solution so prepared was analysed polarographically after deaeration. [Ad.Hu.]

875 – The solubility of manganese ferrocyanide in water and aqueous solutions (in Polish). A. Basiński and M. Pasgreta (Dept. of Physical Chemistry, Kopernik University, Toruń, Poland). *Roczniki Chem.*, 34 (1960) 41.

The solubility of manganese ferrocyanide was determined at 25° in water and aqueous solutions of HCl, HNO_3 , acetone, methanol and ethanol in varying concentrations. In water the solubility was found to be $2.27 \cdot 10^{-5}\text{ M}$ and $2.40 \cdot 10^{-5}\text{ M}$ respectively by the polarographic and colorimetric

methods used for the determination of the manganese concentration in a saturated solution of $\text{Mn}_2[\text{Fe}(\text{CN})_6]$. In HCl and HNO_3 the solubility increased at pH 3 and 4 respectively. Addition of about 30% v/v of organic solvent decreased the solubility to approx. $1 \cdot 10^{-5} M$, with no further decrease at higher contents of organic solvents. [Ad.Hu.]

876 – The solubility of nickel ferrocyanide in water and aqueous solutions (in Polish). A. Basiński and M. Rozwadowski (Dept. of Physical Chemistry, Kopernik University, Toruń, Poland). *Roczniki Chem.*, 34 (1960) 47.

The solubility of nickel ferrocyanide was determined at 25° in water and in aqueous solutions of HCl , HNO_3 , acetone, methanol and ethanol in varying concentrations. In water the solubility was found to be $2.67 \cdot 10^{-5} M$ and $2.50 \cdot 10^{-5} M$ respectively by the polarographic and colorimetric methods used for the nickel determination in a saturated $\text{Ni}_2[\text{Fe}(\text{CN})_6]$ solution. In HCl and HNO_3 solutions the solubility increased at about pH 3, increasing amounts of organic solvents decreasing the solubility. [Ad.Hu.]

877 – The application of a hanging mercury drop electrode to the investigation of the properties of complex amalgams (in Polish). W. Kemula and Z. Galus (Dept. of Inorganic Chemistry, University of Warsaw, Poland). *Roczniki Chem.*, 34 (1960) 251.

The intermetallic compounds Ni–Sn and Ni–Zn were studied in mercury by means of the hanging mercury drop electrode. This investigation was performed in 0.5 N NaF using the anodic polarisation curves of the amalgams formed during the electrolysis of solutions of the corresponding cations. Anodic oxidation of the first amalgam produced two minima, at -0.7 and -0.4 V, which corresponded to $\text{Sn} \rightarrow \text{Sn}^{2+} + 2e$ and $\text{Sn}^{2+} \rightarrow \text{Sn}^{4+} + 2e$ reactions respectively. In the presence of nickel these minima decreased to give one minimum at 0 V corresponding to the intermetallic compound of Ni–Sn. To establish the composition of this compound $2.5 \cdot 10^{-4} N$ SnCl_2 solutions with increasing concentrations of added nickel were electrolysed and anodically oxidised. The Ni : Sn concentration ratio was plotted vs. minimum depth. The intersection of this line with the [Ni] : [Sn] axis gave the concentration ratio 2 : 1 in the electrolysed solution. Taking into account the diffusion coefficient ratio of ions, equal to 1 : 2, which corresponds to the ratio of metals passing into the mercury, the atomic ratio in the intermetallic compound was found to be equal to 1 : 1.

The same procedure was used to determine the composition of the Ni–Zn compound, which was found to be 1 : 1. Formation of these relatively stable compounds can influence the results of analytical determinations. It was suggested that in these cases a metal should be introduced which forms a more stable compound with the interfering metal. As an example the Zn–Sn–Ni system was given. When the Zn–Sn amalgam was anodically oxidised in the presence of small amounts of Ni in mercury only the more stable SnNi was formed, without any disturbance of the Zn oxidation minimum. [Ad.Hu.]

878 – Distinction between the kinetic currents due to an acid recombination or to an acid-catalyzed reaction (in English). E. T. Bartel, Z. R. Grabowski and W. Kemula (Dept. of Inorganic Chemistry, University of Warsaw, Poland). *Roczniki Chem.*, 34 (1960) 345.

Distinction between the current caused by an acid recombination, and that due to an acid-catalysed tautomerisation is based on the fact that the tautomeric equilibrium constant does not involve hydrogen ion activity. For acid recombination

$$\log \frac{i_k}{i_a - i_k} = pK' - \text{pH}$$

where $K' = 1.13 \sqrt{K/k_2}$, but for acid catalysis

$$\log \frac{i_k}{i_a - i_k} = \frac{1}{2}(pK' - \text{pH})$$

where $K' = 1.28 K/k_2$. This criterion can be readily found graphically by plotting $\log i_k/(i_a - i_k)$ vs. pH and calculating the slope of the line. On this basis the kinetic current of *p*-hydroxybenzaldehyde was ascribed to an acid recombination reaction, rejecting the previously accepted (E. T. Bartel, Z. R. Grabowski, W. Kemula and W. Turnowska-Rubaszewska, *Roczniki Chem.*, 31 (1957) 27) hypothesis of tautomerisation. [Ad.Hu.]

879 – Contribution au problème de l'électrode à membrane (en allemand). P. Bersier, J. Bersier et F. Hügli (Technicum de Winterthur, Suisse). *Helv. Chim. Acta*, 42 (1959) 2514.

Des titrations de précipitation au sulfate ont été étudiées avec des membranes d'oxyde d'aluminium.

Les sauts de tension de membrane de quelques titrations y sont décrits. Cette méthode peut être utilisée pour la détermination des points équivalents. [De.Mo.]

880 – Etude analytique du cobalt au polarographe à rayons cathodiques. D. Monnier, J. Vogel, W. Haerdi et P. E. Wenger (Laboratoires de chimie minérale, de chimie analytique et de microchimie, Université de Genève, Suisse). *Helv. Chim. Acta*, 42 (1959) 1672.

Une étude systématique du dosage du cobalt a été faite. Avec le polarographe à rayons cathodiques, on peut encore déterminer 0.1 $\mu\text{g}/\text{ml}$ de cobalt dans un volume de 0.1 ml, soit en quantité absolue 0.01 μg de cobalt. Une étude statistique de l'erreur est présentée.

L'oxygène gêne le dosage, car en présence de cobalt et d'un chlorure, il donne un saut inattendu à -1.4 V, alors que celui de cobalt disparaît. Le zinc qui se trouve en quantité appréciable dans les acides nitrique et perchlorique, donne un saut qui se superpose à celui du cobalt. On peut ramener le saut du zinc à sa tension ordinaire en traitant le résidu par l'acide chlorhydrique.

La dithizone doit être entièrement détruite car elle donne un saut polarographique dans le voisinage de celui du cobalt. Une méthode de destruction de cette dernière est proposée. [De.Mo.]

881 – The polarographic determination of hexavalent uranium in the presence of excess ferric iron.

A. A. Verbeek, J. T. Moelwyn-Hughes and E. T. Verdier (Dept. of Chemistry, University of Natal, Pietermaritzburg, South Africa). *Anal. Chim. Acta*, 22 (1960) 570.

It is shown that concentrations of uranyl ions varying from 10^{-4} M to 10^{-3} M may be rapidly determined polarographically with an accuracy of 4% (95% confidence) in the presence of concentrations of ferric iron up to one hundred times that of the uranyl ion concentration. The determination is insensitive to the concentration of the 0.75 M sodium fluoride used as the supporting electrolyte and to time, but is not valid if the pH of the test solution is below 6.5. The ions Cu^{2+} , Pb^{2+} and Mn^{2+} are shown not to interfere, while Ti^{3+} must be removed.

The method should prove applicable to the determination of uranyl ions in the "pregnant liquors" of the uranium mining industry. [P.Me.]

882 – The behaviour of pyro- and tripolyphosphate complexes at the dropping mercury electrode.

P. R. Subbaraman and P. S. Shetty (National Chemical Laboratory, Poona, India). *Anal. Chim. Acta*, 22 (1960) 495.

The half-wave tensions for the cathodic waves of some metals obtained in aqueous pyrophosphate and tripolyphosphate are reported. All the metals give single steps which are well-developed and free from maxima. At pH 5 the wave for lead is reversible in both the phosphates. Waves for the other metals (Bi, Ti and Nb), including those for lead at pH 7, are all irreversible. It may be observed that the differences between the half-wave tensions of the simple metal ions, lead, bismuth and titanium and those of their respective complexes are slightly more for the tripolyphosphate complexes than for the pyrophosphate complexes. [P.Me.]

883 – The simultaneous determination of copper and iron in high purity aluminum using the K 1000 cathode ray polarograph. J. Hetman (Southern Instruments Ltd., Camberley, Great Britain).

Anal. Chim. Acta, 22 (1960) 394.

An accurate simultaneous determination of copper and iron in 99.99% aluminum can be carried out in 10–15 min using the linear sweep polarograph. Lead can also be determined in the same solution. The basic electrolyte used is a mixture of sodium hydroxide and sucrose but the addition of ethylenediaminetetraacetic acid (EDTA) is necessary if manganese is present. The effect of EDTA on the reduction wave of copper and iron has been investigated. The present method is very rapid, totally eliminating chemical manipulations such as filtering, extraction, etc., and enables the simultaneous estimation of copper and iron with a tolerance of $\pm 0.0001\%$ for copper contents $< 0.005\%$, $\pm 0.00001\%$ for iron contents of $< 0.0001\%$ and $\pm 0.0001\%$ for iron contents between 0.0001% and 0.005%. [P.Me.]

884 – Amperometric determination of zirconium(IV) with tartrazin (in German). Gr. Popa, D.

Negoiu and Gh. Baiulescu (Laboratory for Inorg. and Anal. Chem., Faculty of Chem., University C.I., Parhon, Bucharest, Rumania). *Anal. Chim. Acta*, 22 (1960) 200.

The authors have shown, in a previous paper (*Anal. Chim. Acta*, 21 (1959) 33) that tartrazin can be used for the gravimetric determination of zirconium. The formula of the complex is Zr_3 (tartrazin) $(\text{OOH})_3$. The same complex can be used for the amperometric determination of zirconium. The titration can be performed in the presence of uranium(VI). For uranium quantities of up to 39 times those of zirconium, the error is 2%. [P.Me.]

885 – Amperometric titration of albumin in blood serum by copper(II). I. M. Kolthoff, B. R. Willeford Jr. and D. Singh (School of Chemistry, University of Minnesota, Minneapolis, Minn., U.S.A.).

Anal. Chim. Acta, 22 (1960) 92.

It is shown that in ammoniacal buffer of pH 9.2, copper(II) reacts with bovine serum albumin in a mole ratio of one to one but does not react with human γ -globulin under similar conditions. Because of the structural similarity of bovine serum albumin to human serum albumin, these results suggest that the reaction of copper(II) with albumin can be made the basis for an amperometric titration of albumin in blood serum with copper(II). This titration yields values in essential agreement with, but in general somewhat lower than, those obtained by precipitation in 28% sodium sulfite solution. [P.Me.]

886 – The determination of uranium by cathode-ray polarography. E. Booth and E. A. Terry (U.K.A.E.A. Research Group, Chemistry Division, Woolwich Outstation, London, Great Britain). *Anal. Chim. Acta*, 22 (1960) 82.

An electrolyte 1 *M* with respect to perchloric acid and 0.01 *M* with respect to hydrochloric acid forms a very satisfactory base for the determination of uranium by either conventional or cathode-ray polarography. Accurate control of the acidity of the base solution is unnecessary. The only element which causes serious interference is molybdenum.

For the c.r. polarograph the calibration is linear over the range $2 \cdot 10^{-6}$ – $4 \cdot 10^{-3}$ *M* uranium. At a uranium concentration of $4 \cdot 10^{-5}$ *M* the coefficient of variation of the results from a Cambridge polarograph is 1.8% and that for the c.r. polarograph is 1.5%. At a uranium concentration of $4 \cdot 10^{-4}$ *M* these figures are 1.8% and 1.3% respectively. [P.Me.]

887 – Amperometric titration of boron with fructose. W. B. Swann, W. M. McNabb and J. F. Hazel (Dept. of Chemistry, University of Pennsylvania, Philadelphia, Pa., U.S.A.). *Anal. Chim. Acta*, 22 (1960) 76.

Aqueous solutions of borate can be titrated amperometrically with standard fructose solutions. This procedure may be used to determine the boron content of various types of samples after conversion of the boron to the borate form. The method is based upon the observation that the polarographic wave of fructose in a 0.1 *M* LiCl, 0.01 *N* LiOH solution is depressed by the presence of borate ions. The interference due to the reduction of cations at more positive tensions than the fructose (–2.05 V) may be removed very conveniently by passing the sample through the hydrogen form of a cation-exchange resin. Commonly-occurring anions do not interfere. Under the prescribed conditions the method is sensitive to a few hundredths of a milligram of boron. [P.Me.]

888 – Über die Wirkungsweise von Inhibitoren bei polarographischen Reduktionen organischer Verbindungen. B. Kastening und L. Holleck (Institut für Physikalische Chemie der Universität Hamburg, Deutschland). *Z. Elektrochem.*, 64 (1960) 823.

Es wird die Wirkung von an der Elektrode adsorbierten Inhibitoren auf die Reduktion aromatischer Nitroverbindungen untersucht. Die Inhibitionswirkung tritt vor allen in alkalischem Milieu hervor, wenn das primäre Reaktionsprodukt als Anion vorliegt; die Reaktionsgeschwindigkeit ist dann um Größenordnungen herabgesetzt. Das neutrale ursprüngliche Depolarisationsteilchen erfährt keine Reduktionshemmung, desgleichen das Radikalanion, wenn es bei niedrigen pH-Werte durch Protonenaufnahme in ein neutrales Radikal übergehen kann.

Von den untersuchten Inhibitoren zeigen Tylose und Pyridin ein abweichendes Verhalten. Für diese Fälle werden spezielle Inhibitionsmechanismen diskutiert. [Ha.Re.]

889 – Der Einfluss der Puffersäure auf die reaktionskinetisch bedingte polarographische Stromstärke. M. Becker und H. Strehlow (Max-Planck-Institut für Physikalische Chemie, Göttingen, Deutschland). *Z. Elektrochem.*, 64 (1960) 818.

Es werden die Schwierigkeiten diskutiert, die bei der polarographischen Bestimmung von Rekombinationsgeschwindigkeiten bei α -Oxocarbonsäuren durch Pufferbestandteile der Lösung hervorgerufen werden. Die Puffersäure kann an die Säureanionen Protonen abgeben, und die der Reduktion vorgelagerte Rekombination kann infolge dünner Reaktionsschichten einen heterogenen Charakter annehmen. Es werden auf diese Weise zu hohe Reaktionsgeschwindigkeiten vorgetauscht. Polarographische Bestimmungen von Rekombinationsgeschwindigkeiten der Brenztraubensäure und der Phenylglyoxylsäure in imidazol- und imidazolchloridhaltigen Phosphatpuffern werden beschrieben. [Ha.Re.]

890 – Der Einfluss der Hydratbildung auf das polarographische Verhalten von α -Oxocarbonsäuren. M. Becker und H. Strehlow (Max-Planck-Institut für Physikalische Chemie, Göttingen, Deutschland). *Z. Elektrochem.*, 64 (1960) 813.

Polarographisch bestimmte Rekombinationsgeschwindigkeiten von α -Oxocarbonsäuren können durch der Elektrodenreaktion vorgelagerte Reaktion von komplizierten Verlauf, durch Parallelreaktion, sowie durch nicht homogen verlaufende Vorreaktionen um Größenordnungen verfälscht sein. Es wird an hand der Ultraviolett durchlässigkeit und polarographischer Messungen der

Einfluss der Hydratbildung auf die polarographischen Geschwindigkeitskonstanten von Brenztraubensäure und Glyoxylsäure untersucht. [Ha.Re.]

891 – Polarographic investigation on a stilbene-ditetrazolium compound (in German). G. Horn and B. Jambor (Institute for Microbiology, Jena, East Germany). *Contrib. Polarog.*, Vol. IV, Suppl. to *Ricerca sci.*, 30 (1959) 173.

A new stilbene-ditetrazolium compound has been prepared and polarographically examined. The reduction products of this compound appear to be quite insoluble in lipids. The influence of varying both pH and concentration on its polarographic characteristics is investigated over a wide range. Its behavior is quite similar to that of neotetrazolium and tetrazolium blue also prepared by Kivalo and Mustakallio. The same values of half-wave tension are observed for the compound investigated and neotetrazolium, while the tetrazolium blue steps are shifted to more negative tensions by nearly 100 mV. [Fr.Pan.]

892 – Polarography of 3,5-dinitrobenzoic acid and its sterol-esters (in German). H. Berg and H. Venner (Institute for Microbiology, Jena, East Germany). *Contrib. Polarog.*, Vol. IV, Suppl. to *Ricerca sci.*, 30 (1959) 181.

A double wave is observed when polarographically studying buffered solutions of 3,5-dinitrobenzoic acid. The limiting current is diffusion-controlled and proportional to the depolarizer concentration. An oscillographic examination of the curve dE/dt vs. E has also been performed. Polarographic data are given for the esters of vitamin D₂, lumisterol, ergosterol, suprasterol, cholesterol and pyridine containing lumisterol ester adduct, in a solution of 80% dioxane. In the case of the luminol ester, polarographic and spectroscopic data indicate the presence of an intramolecular compound. [Fr.Pan.]

893 – Structure and polarography of complex ions (in Italian). G. Sartori (Istituto di Chimica, University of Trieste, Italy). *Contrib. Polarog.*, Vol. IV, Suppl. to *Ricerca sci.*, 30 (1959) 229.

Weak and inert complex species have been examined and several methods, such as isotopic exchange, substitution and isomerization give evidence on the ease with which they can be transformed: some examples are given. Inner complexes are polarographically reduced in a reversible way, provided that the $(n - 1)d$ atomic orbital can accept the electron, no matter whether the complex is inert or weak. Outer complexes are only reversibly reduced if they are weak; when the electron transfer involves an electronic change in the structure, the reduction appears to be irreversible. Suitable methods in such investigations are: (i) transitometry, which shows the reaction occurring either before, at the same time as, or after cathodic reduction; (ii) Gerischer methods, which indicate the complex form undergoing the reduction. [Fr.Pan.]

894 – Polarographic determination of free sulphur in oil products (in Italian). G. Zuliani and L. Griggio (Polarographic Center, Padova, Italy). *Contrib. Polarog.*, Vol. IV, Suppl. to *Ricerca sci.*, 30 (1959) 239.

Several mixtures of solvent-supporting electrolytes were investigated in order to determine polarographically the free sulphur in oil fractions. The mixture glacial acetic acid–0.2 M ammonium acetate can be used for the analysis of gasolines and light fractions over the range 0.2–4 mmoles/l sulphur, triton being suitable as the maximum suppressor. Comparative analyses with the lamp method, according to A.S.T.M., show that such polarographic determinations give high accuracy. Determination of sulphur in crude oils and heavy fractions is better carried out in a 50% methanol–50% benzene solution with 0.1 M acetate buffer. [Fr.Pan.]

895 – Vanadium determination in oil products (in Italian). G. Zuliani, A. Delmarco and G. Milazzo (Centro di Polarografia, Padova, Italy). *Contrib. Polarog.*, Vol. IV, Suppl. to *Ricerca sci.*, 30 (1959) 247.

Some electrochemical and volumetric methods, suitable for semi-micro-determinations of V, mainly in oil products, have been developed or controlled. After ignition of the sample and solubilization with H₂SO₄, the interfering elements are eliminated by reduction at a Hg cathode; a suitable volume is oxidized with H₂O₂ and treated with hot Na₂SO₃ to obtain V(IV); this solution is mixed with the supporting electrolyte (1 N OH⁻ plus 0.1 M Na₂SO₃) and polarographically examined. The anodic diffusion current, corresponding to a 1-electron oxidation, is measured at -0.25 V/S.C.E., i_d being proportional to V concentration in the range 3–65 p.p.m.

In volumetric determinations of V(V) with Fe(II) or hydroquinone, the end-point can be observed either by *o*-dianisidine or potentiometrically or by the dead-stop method: the latter allows the determination of 2.5 μg of V ± 10% in 5 ml. [Fr.Pan.]

896 – Polarographic determination of reagent purity: polarographic behavior of some elements in 2 N HCl (in Italian). E. Fornasari and E. Gagliardo (Polarographic Center, Padova, Italy). *Contrib. Polarog.*, Vol. IV, Suppl. to *Ricerca sci.*, 30 (1959) 257.

The half-wave tensions and diffusion current constants are given for 20 elements in 2 *N* HCl. Bi, Cd, In, Pd, Sn, Tl and Cu yield well-defined polarographic steps suitable for analytical purposes. The behavior of As, Co, Re and U is quite complex and their waves can hardly be used for quantitative determination. 49 references are given. [Fr.Pan.]

897 – Polarographic determination of reagent purity: polarographic behavior of some elements in 2 *N* HNO₃ (in Italian). E. Fornasari and B. Tosini (Polarographic Center, Padova, Italy). *Contrib. Polarog.*, Vol. IV, Suppl. to *Ricerca sci.*, 30 (1959) 267.

In a nitric acid solution no reduction step is observed for Cd, In, Re, Sn and Ti before the discharge of the supporting electrolyte. Ag, Cr(VI), Hg, Fe and V yield diffusion currents at zero applied tension. Almost similar behavior is observed with Au. Well-developed waves are obtained with Bi, Cu, Pb, Sb, Tl and U, suitable for analytical determinations. As and Co yield ill-defined steps. 42 references. [Fr.Pan.]

898 – Applications of polarography in the oil industry: subject index (in Italian). G. Zuliani (Polarographic Center, Padova, Italy). *Contrib. Polarog.*, Vol. IV, Suppl. to *Ricerca sci.*, 30 (1959) 303. A review, in the form of a subject index, of polarographic works concerning the products of oil industry. References are given in accordance with numbers of the polarographic bibliography published by the Center of Polarography C.N.R., Padova, Italy. [Fr.Pan.]

899 – The kinetic parameters of the polarographic O₂ reduction in the presence of substances adsorbed on the electrode (in Italian). P. Silvestroni and L. Rampazzo (Institute of General Chem., University of Perugia, Italy). *Ricerca sci.*, 30 (1960) 260.

Polarographic reduction curves from alkaline O₂ solutions were recorded in the presence of substances such as eosin, ethyl-orange, etc., which can be adsorbed on the electrode. The usual apparatus, an undamped galvanometer and a 15–20 sec dropping capillary were used. Absorption phenomena occurring during the drop life were investigated. Tables are given of the values of kinetic parameters concerned with the O₂ reduction and the shift of $E_{1/2}$ with increasing concentration of the adsorbed substances is taken into account. [Fr.Pan.]

900 – A polarographic investigation on palladium complexes with pyridinic bases (in Italian). F. Pantani (Institute of Anal. Chemistry, University of Florence, Italy). *Ricerca sci.*, 30 (1960) 849. A well-defined polarographic step is obtained in the range -0.3 to -0.4 V/S.C.E. with pyridine or picoline solutions of Pd²⁺, maxima being suppressed by methylene blue. The electrode process is irreversible and consists of a 2-electron reduction. Determinations of 0.1–5 m/moles/l Pd²⁺ can be performed and the interference due to Ir, Pt, Au and Rh is investigated.

For ligand concentrations lower than 0.01 *M*, two steps may appear, owing to the presence of two differently coordinated forms. With increasing temperature or mercury height, variations of the polarographic characteristics in accordance with steric hindrance between the ligand molecules may be observed. [Fr.Pan.]

901 – The determination of silver, cadmium, indium and tin in silver-base alloys. D. P. Stricos and J. T. Porter (Knolls Atomic Power Lab., General Electric Co., Schenectady, N.Y., U.S.A.). *U.S. Atomic Energy Commission TID-7568*, Pt. 1, (1959) 233.

0.25 g of the sample are dissolved in a mixture of fluoboric and nitric acids with gentle heating. After dilution, silver is precipitated with 10 ml of 0.2 *M* HCl and gravimetrically analyzed as AgCl in the usual way. The solution is evaporated and two aliquots are taken. The first is diluted with KI and polarographically analyzed for In and Cd. The $E_{1/2}$ values in 1 *M* KI are -0.57 V/S.C.E. for In and -0.75 V for Cd: the steps are separated sufficiently to allow the two elements to be determined simultaneously.

HCl and NH₄Cl are added to the second aliquot in order to obtain a final solution 1 *M* in HCl and 4 *M* in NH₄Cl. A polarographic step at -0.55 V is produced by tin in this medium and this may be suitable for the determination of such an element. The diffusion current plateau is partly concealed by the following indium wave and measurements of i_d are better performed 0.05 V to the right of the half-wave. [Fr.Pan.]

902 – The indirect assay of uranium tetrafluoride by the polarographic determination of uranyl fluoride. T. J. Kneip and J. D. Dowdy (Mallinckrodt Chem. Works, Uranium Div., St. Charles, Mo., U.S.A.). *U.S. Atomic Energy Commission TID-7568*, Pt. 1, (1959) 224.

The determination of the UO₂F₂ content in UF₄ by various leaching procedures as well as by calculation of the difference between total U and U(IV) involve large errors. A procedure is proposed for the polarographic determination of UO₂F₂ up to 6% in the presence of excess UF₄. A well-defined step is obtained in 0.5 *M* ammonium oxalate with $E_{1/2} = -0.43$ V/S.C.E.; the diffusion current is read at -0.55 V. The electrode process might appear to be a one-electron reduction

to U(V) but more complex phenomena also occur, owing to the fast disproportionation of this species into U(IV) and U(VI). The interference of V, Ce, Fe and U₃O₈ is briefly investigated.

[Fr.Pan.]

903 – Polarographic characteristics of ammonium ion and ammonia. C. J. Nymann, J. L. Ragle and P. F. Linde (Dept. of Chemistry, Washington State University, Pullman, Wash., U.S.A.). *Anal. Chem.*, 32 (1960) 352.

The polarographic behavior of the ammonium ion during reduction in the pH region from 4 to 13 in tetramethylammonium iodide and hydroxide is investigated. The electrode reaction is diffusion controlled. The diffusion constants obtained polarographically agree with the calculated ones. In an acidic medium the wave is irreversible, but in basic solutions the wave is due to a reversible one-electron reduction to ammonium amalgam and hydroxide. Typical polarograms are shown. The variation of the half-wave potential as a function of the pH is studied and interpreted.

[Kl.Gr.]

904 – Polarographic determination of styrene monomer in polyester resins. W. M. Ayres and G. C. Whitnack (Chem. Div. Research Dept., U.S. Naval Ordnance Test Station, China Lake, Calif., U.S.A.). *Anal. Chem.*, 32 (1960) 358.

A solution of the resin in ethyl alcohol is polarographed in a tetrabutylammonium chloride supporting electrolyte. A 250–500 mg sample of the resin is shaken for 1 h with 50 ml ethyl alcohol in a 100 ml volumetric flask. The flask is made up to the mark with alcohol and a 5 ml aliquot is added to a 30 ml polarographic beaker containing 5 ml 0.1 M tetrabutylammonium chloride solution and 10 ml 95% alcohol. The polarogram is obtained from –2.0 to –2.8 V. Dissolved oxygen need not be removed. The analysis has a precision of 5 parts per 1000.

[Kl.Gr.]

905 – Polarographic behavior of aryl sulfones and sulfoxides. R. C. Bowers and H. D. Russel (Dept. of Chemistry, Northwestern University, Evanston, Ill., U.S.A.). *Anal. Chem.*, 32 (1960) 405.

The polarographic behavior of phenyl methyl sulfone(I), phenyl sulfone(II), phenyl methyl sulfoxide(III), and phenyl sulfoxide(IV) is investigated. All the four compounds give well-defined waves in the concentration range from 1 to 6 mM. At concentrations above 2 to 3 mM a noticeable break in the waves is observed. The limiting currents vary linearly with concentration in all cases. The half-wave tension data are: I, –2.14; II, –2.04; III, –2.18; IV, –2.07 V vs. S.C.E. The number of electrons in the electrode reaction is 2, as observed from controlled tension coulometry. The reduction products are determined by spectral identification. They are the corresponding sulfuric acids and thioethers.

[Kl.Gr.]

906 – Investigation of processes in organic chemistry with the use of oscillographic polarography. I.

K. Molnarova and L. Molnar (Institute for Chemistry, Slovak Academy of Sciences, Bratislava, Czechoslovakia). *Acta Chim. Acad. Sci. Hung.*, 18 (1959) 93.

On observing the anomalous behaviour of narcotene and hydrastine in alkaline electrolytes, the authors presumed the occurrence of chemical alterations in these compounds, namely cleavage of the lactone ring. The analysis of the isolated salts of narcotic acid indicated that actually a structural change takes place due to the cleavage of the lactone ring. Values of the depolarisation tension of narcotene, hydrastine and of the salts of their hydroxy acids in various electrolytes on the mercury electrode are given by the authors. The cleavage of the lactone ring was plotted against time, on the basis of data established by oscillographic polarography.

It was found that the experiments could also be reproduced with a streaming electrode using the primary curve, and that the results obtained are in accordance with the values established by the dropping mercury electrode.

[E.Juh.]

907 – The mechanism of the polarographic reduction of kotarnin (in German). K. Györbiró (Institute of Inorganic Chemistry, Technical University, Budapest, Hungary). *Periodica Polytech.*, 4 (1960) 61.

Verfasser stellt auf Grund weiterer Untersuchungen des polarographischen Verhaltens des Kotarnins und einiger Kotarnin-analoga für die polarographische Reduktion des Kotarnins einen neuen Reduktionsmechanismus auf. Nach diesem ist die polarographisch aktive Form das Kotarninium Kation, das an der Quecksilber-Tropfelektrode in saurer Lösung in einer einzigen 2-Elektronen-Phase und in neutralem und alkalischem Medium in zwei Phasen mit je einem Elektronenübergang an Hydrokotarnin reduziert wird. In von organischen Lösungsmitteln freier wässriger Lösung können sich die Stufen infolge der stärkeren Adsorptionskräfte und der geringeren Löslichkeit verzerren. Bei diesem Mechanismus der Reduktion muss die Teilnahme nicht dissoziierter Kotarninmoleküle im Elektrodenprozess nicht angenommen werden, die Gegenwart der Aminoaldehyd Form des Kotarnins ist demnach nicht als polarographisch bewiesen zu betrachten.

[E.Juh.]

908 – The possibility of determination of dissociation-constants by catalytic waves (in German). E. Pungor and E. Rokosinyi-Hollós (Institute of Inorganic and Analytical Chemistry, L. Eötvös University, Budapest, Hungary). *Acta Chim. Acad. Sci. Hung.*, 22 (1960) 69.

Der Untersuchungen gemäss kann die Dissoziationskonstante von stickstoffhaltigen organischen Verbindungen durch Polarographie in jenem Sinne nicht bestimmt werden, wie man es nach der Mitteilung von Knobloch erwartete. Verfasser sind jedoch der Meinung, dass jene Feststellung von Knobloch richtig sei, nach welcher man im Falle der erwähnten Verbindungen die Dissoziationskonstante durch die katalytische Wasserstoffwelle bestimmen kann. Die auf diese Weise ermittelte Dissoziationskonstante ist aber der in einer homogenen Phase messbaren Konstante nicht gleich, ihr Wert durch die in der Umgebung der Elektrodenoberfläche herrschenden Verhältnisse beeinflusst. [E.Juh.]

909 – Salts of quinol-pyridine. VI. Formation of semiquinones in the polarographic reduction of quinone-pyridine salts (in Italian). G. Faraone and M. Trozzi (Institute of Phys. Chemistry, University of Milan, Italy). *Ann. chim. (Rome)*, 49 (1959) 1916.

The redox system of the salts derived from quinol-pyridine and quinone-pyridine is investigated polarographically. The behaviour is quite similar to that of the quinone-hydroquinone system: both cathodic and anodic steps are reversible and correspond to a two-electron process; two H⁺ ions are also involved in the redox reaction. Evidence is given for the presence, in slightly alkaline solutions, of a semiquinone as an intermediate product of the reduction of the quinone-pyridine salts. [Fr.Pan.]

910 – Amperometric determination of sulphhydryl content of blood and tissues. S. K. Bhattacharya (Dept. of Biochemistry, University of Leeds, Great Britain). *Nature*, 183 (1959) 1327.

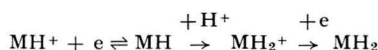
Most of the methods available for determining non-protein and protein sulphhydryl contents of biological materials are rather complicated. In this study the amperometric method of Benesch, Lardy and Benesch can be used with a slight modification for the specific determination of the total sulphhydryl content of biological material. The amperometric titration apparatus with the exception of the platinum electrode is assembled according to Benesch, Lardy and Benesch. The platinum electrode is made of four strands of tightly-twisted platinum wire sealed in soft glass in a special way. Tissue homogenate, whole blood and sulphosalicylic acid extracts of blood and tissues are titrated with 0.002 M silver nitrate in tris-aminomethane buffer pH 7.4. The increments of silver nitrate are added at one min intervals and the microammeter reading is taken at 55 sec after each addition. Special treatment and precautions have to be made before and during the titration. [M.K.Hus.]

911 – Influence of nitrogen-containing bases on the rate of the electrode processes at the dropping mercury electrode. V. Volkova (Polarographic Institute, Czechoslovak Academy of Science, Prague, Czechoslovakia). *Nature*, 185 (1960) 743.

Polarographic studies have shown that gelatin, amines, *p*-aminobenzoic acid, esters of amino-alcohols and nitrogen-containing heterocyclic compounds such as various pyridine derivatives, have reducing effects on substances capable of dissociation. This effect manifests itself in the polarograms either by changing the wave-height due to any anion recombination with the nitrogen-containing cation as proton donor, or by shifting the potentials towards more positive values. The *i-t* curves show that these catalysts have a strong adsorptive character which reveals itself by accelerating the electrode processes. This acceleration is explained on the basis of a cationic adsorption of the surface-active substances. [M.K.Hus.]

912 – The polarographic reduction of aromatic hydrocarbon positive ions and proton complexes.

W. I. J. Aalbersberg and E. L. Mackor (Koninklijke/Shell-Laboratorium (Shell Internationale Research Maatschappij N.V.), Amsterdam, The Netherlands). *Trans. Faraday Soc.*, 56 (1960) 1351. The polarograms obtained in solutions of perylene, tetracene, anthracene, 3,4-benzopyrene, pyrene and 1,2-benzanthracene in strongly acid mixtures of CF₃COOH and H₂O·BF₃ (20%) generally manifest two waves. The first wave corresponds to the one-electron reduction of the hydrocarbon positive ion, M⁺ + e ⇌ M followed by M + H⁺ → MH⁺. The second wave is attributable to a two-electron process involving the reduction of the proton complex:



Proton complexes of the cata-condensed hydrocarbons are reduced more easily than those of the peri-condensed hydrocarbons. The difference in half-wave tension (~0.3 eV) is explained, after calculating the π-electronic energies of these ions, by using the theory of Hash and Pople which includes electron interaction. [M.K.Hus.]

913 – Determination of chemically combined iodine in sea water by amperometric and catalytic methods. R. A. Barkley and Th. G. Thompson (Dept. of Oceanography, University of Washington, Seattle, Wash., U.S.A.). *Anal. Chem.*, 32 (1960) 154.

The amperometric method of Potter and White is used for the determination of traces of iodine in sea water. The instrument allows the determination of $5 \cdot 10^{-7} M$ concentrations of iodine present in the water. Titration is carried out with thiosulfate in 0.25% acetic acid. A tension of about 0.3 V is applied to the two platinum wire electrodes. The solution is deaerated with nitrogen and titrated with a 0.002 N thiosulfate solution which is prepared daily. The standard deviation is 2.1 gamma per liter. [Kl.Gr.]

914 – Automatic recording of dissolved oxygen in aqueous systems containing surface active agents. K. H. Mancy and D. A. Okun (Dept. of Sanitary Engineering, School of Public Health, University of North Carolina, Chapel Hill, N.C., U.S.A.). *Anal. Chem.*, 32 (1960) 108.

A method is described for continuous polarographic recording of dissolved oxygen. The apparatus permits the circulation, aeration and deaeration of the sample stream. The effect of adsorption of surface active agents, such as Aerosol OT and alkyl benzene sulfonate of the anionic type, coconut fatty alkyl benzyl dimethylammonium chloride of the cationic type, and Triton X 100 of the non-ionic type on the reduction of oxygen, has been studied. The adsorption of anionic compounds on the dropping mercury electrode interferes in the region of the first oxygen wave and the cationic compounds in the region of the second oxygen wave. Non-ionic compounds interfere throughout the entire range of applied voltage. A manual polarograph with a pen recorder and a cathode ray oscillograph are used for the investigation of the electrode reactions. [Kl.Gr.]

915 – Polarographic determination of alpha-methyl-DL-cystine. R. J. Thibert and R. M. Ottenbrite (Dept. of Chem., Essex College, Assumption University of Windsor, Ontario, Canada). *Anal. Chem.*, 32 (1960) 106.

The polarographic determination of alpha-methyl-DL-cystine in 0.1 N hydrochloric acid, using thymol as a maximum suppressor is investigated. The relationship between the concentration of the compound, the temperature and the diffusion current is studied. The influence of thymol concentration and pH on the half-wave value is determined. A linear relationship between the diffusion current and the concentration in the range of $5 \cdot 10^{-4}$ to $2 \cdot 10^{-3} M$ is observed. The drop rate is adjusted to 3 sec. [Kl.Gr.]

916 – Cathodic action of the phenylenediamine dihydrochlorides at the dropping mercury electrode. S. R. Cooper and O. F. Fowlkes (Howard University, Washington, D.C., U.S.A.). *Anal. Chem.*, 32 (1960) 26.

o-Phenylenediamine dihydrochloride gives a single polarographic wave in a 0.1 M supporting electrolyte of tetramethylammonium bromide with gelatine as the maximum suppressor while the *para* compound gives two waves. The wave of the *meta* compound is very similar to that of the *ortho* compound but at a higher concentration it also gives a double wave. The half-wave values vary between -1.43 and -1.52 V. The total height of the waves is a linear function of the concentration. The drop-time is adjusted to 6 sec. The diamines do not give a cathodic wave without hydrochloric acid. The concentration range investigated is 0.5 to $6 \cdot 10^{-3} M$. [Kl.Gr.]

917 – Détermination volumétrique du manganèse, selon la méthode de Lingane et Karplus, dans les fontes et les aciers. J. F. W. Tertoolen, C. Buijze et G. I. Van Kolmeschate (Analytisch Instituut T.N.O., Delft, Pays-Bas). *Chim. anal.*, 42 (1960) 9.

Le manganèse II est dosé par volumétrie. La réaction chimique utilisée est l'oxydation de l'ion Mn^{2+} en $M(III)$ en milieu pyrophosphorique par le permanganate. La fin de la réaction est mise en évidence par la méthode "dead stop"; les électrodes utilisées, anode et cathode sont en argent. Les éléments d'alliage suivants ne gênent pas; chrome, nickel, molybdène antimoine, et cuivre. L'influence du graphite est éliminée par filtrage avant la dilution, celle du vanadium(IV) par une oxydation préalable par H_2O_2 , ou par addition de fluorure. Le tungstène en petites quantités ne gêne pas. La présence de quantités notables de cobalt ne permet plus de réaliser le titrage. Les auteurs fournissent le schéma du circuit indicateur ainsi qu'un croquis des électrodes d'argent utilisées. [Bad.Lam.]

918 – Comportement des iso et hétéropolyacides en milieu acide. Fr. Chauveau, P. Souchay et R. Schaal (Laboratoire de Chimie P.C.B.IV, Faculté des Sciences de Paris, France). *Bull. soc. chim. France*, (1959) 1190.

Les auteurs déterminent les constantes d'acidité K_1 et K_2 du diacide $Mo_4O_{13}H_2$. Après avoir déterminé le coefficient de partage de cet acide entre l'eau et l'alcool isoamylique (44 en faveur de l'eau) les auteurs déterminent la concentration de l'acide non dissocié $Mo_4O_{13}H_2$ dans la phase aqueuse pour diverses acidités (la concentration de H^+ varie de $12.2 \cdot 10^{-3} N$ à $28.2 \cdot 10^{-3} N$). Pour

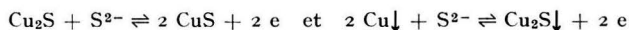
ce faire ils dosent par polarographie le molybdène de la phase organique en équilibre avec l'acide $\text{Mo}_4\text{O}_{13}\text{H}_2$ dans la phase aqueuse. On obtient ainsi la concentration de cet acide dans l'eau. En associant ces déterminations à des mesures de pH, les auteurs obtiennent pour les deux constantes d'acidité les valeurs suivantes: $K_1 = 0.03$ et $K_2 = 0.04$. Ces mesures sont valables en milieu perchlorique car en milieu chlorhydrique ou sulfurique il y a formation de complexes: MoO_2Cl_2 et $[\text{MoO}_3-\text{SO}_4\text{H}_2]\text{H}^+$. Dans la suite de l'article les auteurs étudient le comportement des hétéropolyacides phospho, silico, germano, molybdiques et de l'acide phospho molybdique par spectrophotométrie. [Bad.Lam.]

919 – Réduction électrochimique de suspensions de composés minéraux insolubles. J. Vrebosch et A. Van Tiggelen (Laboratoire de Chimie Inorganique, Université de Louvain, Belgique). *Bull. soc. chim. France*, (1959) 906.

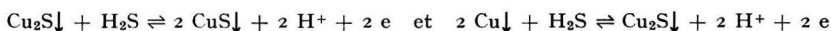
Dans une première partie les auteurs étudient les réactions électrochimiques entre le métal et un sel ou oxyde insoluble adhérant au métal. En premier lieu une étude voltammétrique (tracé des courbes $i = f(E)$) des systèmes $\text{Ag}\downarrow/\text{AgX}$ ($X^- = \text{Cl}^-, \text{Br}^-, \text{I}^-$) indique que ces systèmes sont rapides. Les auteurs interprètent également les courbes tension-temps obtenues au cours d'électrolyse à intensité constante. Ils étudient enfin le rendement de l'électrolyse.

L'étude voltammétrique du système $\text{Cu}\downarrow/\text{CuS}\downarrow$ conduit à admettre l'existence des systèmes rapides suivants:

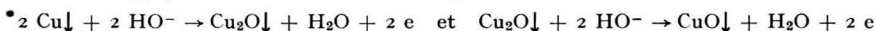
en milieu alcalin



en milieu acide



Les courbes $i = f(E)$ relatives aux réactions d'oxydation



et de réduction



indiquent que ces systèmes sont lents. Les auteurs abordent alors l'étude de la réduction de suspensions de AgCl et CuS . [Bad.Lam.]

920 – Polarographic determination of high concentrations of elements (in Russian). L. N. Lyubimova and V. G. Sotschevanov (Research Institute for Mineral Raw Materials, U.S.S.R.). *Zavodskaya Lab.*, 26 (1960) 703.

The authors have investigated the possibility of determining polarographically elements with concentrations higher than 5%, which is usually recognised as the upper concentration limit, without previous dilution. Deformation of the polarographic curves at high concentrations is caused by a distinct distribution of the polarisation voltages, dependent on the shape of the polarographic vessel and also by changes in the character of the electrochemical process. A polarographic vessel with low resistance has been designed for the determination of Cu, Zn, Cd, Ni and Pb in concentrations of 0.005 to 0.25 M. Results of the determination of Cu, Pb and Zn by chemical and polarographic methods are compared in a table. The error of the result of polarographic determinations according to the described method is about 2%, the concentration of the elements mentioned being 20–30%. [Ot.So.]

921 – Kinetics of the cathodic and anodic polarisation of niobium solutions in various media (in Russian). Ya. P. Gokhstein, L. A. Genkina and A. M. Demkin. *Zhur. Fiz. Khim.*, 34 (1960) 2308. The mechanism of the reduction of niobium and of the oxidation of the products of its electrolysis on the dropping mercury electrode in various media has been investigated. The rate constants and the free activation energies of niobium have been calculated for the first stage of the reduction of Nb(V) and the reverse electrode process in 23 N H_2SO_4 . [Ot.So.]

922 – Polarographic determination of tungsten (in Russian). G. S. Deshnukh and J. P. Srivastava (Baranas Hindu University, Varanasi, India). *Zhur. Anal. Khim.*, 15 (1960) 601. The reduction of hexavalent tungsten on the dropping mercury cathode has been studied using oxalate as the supporting electrolyte. A method has been developed for the successive determination of molybdenum and tungsten in a common electrolyte. The possibility of the separate determination of iron and tungsten has been shown. [Ot.So.]

923 – The question of the mechanism of the electrolytic precipitation of alloys of molybdenum and tungsten with metals of the iron group (in Russian). T. F. Floncevitch-Zabledovskaia, A. N.

Zayats and B. T. Bartschuk (Institute of General and Inorganic Chemistry, Academy of Sciences, U.S.S.R.). *Ukrain. Khim. Zhur.*, 26 (1960) 10.

In an earlier communication the authors mentioned that investigation of polarographic curves makes possible the concept of reactions taking place on the electrode during precipitation of the said alloys. In the previous communication the authors investigated by oscillography the conditions prevailing during the electrolytic precipitation of Ni-Mo and Ni-W alloys from ammoniacal electrolytes. From the oscillograms it was found that the slowest cathode reaction is that of Ni and of its alloys. From both communications (the earlier one was *Ukrain. Khim. Zhur.*, 25 (1959) 713) the mechanism of the cathode reaction in the formation of alloys of Mo and W with elements of the iron group can be elucidated. [Ot.So.]

924 – Polarometric determination of arsenic and antimony (in Russian). V. A. Zacharov, O. A. Songina and N. A. Dragavceva (Kazachian State University, U.S.S.R.). *Zavodskaya Lab.*, 26 (1960) 537.

An amperometric titration is proposed which does not necessitate the separation of As from Sb but which otherwise reacts similarly to the usual method. A rotating platinum and a saturated calomel electrode are used. 2 aliquots of the sample are transferred to beakers, 5 to 10 ml of water are added and the solutions neutralised with sodium bicarbonate. In one beaker the total As and Sb is titrated by 0.01 N I₂ solution at +0.2 V (S.C.E.). Current values are read on the galvanometer 20–30 sec after the addition of the reagent. In the second beaker is placed an amount of 0.01 N K₂CrO₄, equal to 1.5 times the amount of I₂-solution used in the first titration. After 20–30 sec the arsenic is titrated in the same way as before. The amount of iodine needed for the titration of Sb is calculated from the difference. Fe, Cu and Se interfere. At contents of As greater than 2% the error of the determination is 1–5%. [Ot.So.]

925 – Polarometric determination of Bi with trilon B (in Russian). J. I. Usatenko and M. A. Vitkina (F. E. Dzerzhinsky Institute of Chemical Technology, Dnepropetrovsk, U.S.S.R.). *Zavodskaya Lab.*, 26 (1960) 542.

The authors have developed a method for the determination of bismuth under optimum conditions, using amperometric indication with a rotating platinum electrode, in which Trilon B forms a solid complex with Bi. The determination is carried out at pH 1–2. The influence of Cd and Pb in the determination of Bi in alloys of the type of Rose's metal is such that Cd does not interfere since it forms a complex of $pK = 16.1$. Pb forms a complex of $pK = 17.6$ and does not interfere up to ratios of Bi : Pb of 3 : 1. Sn does not interfere but passivates the electrode. Titrations are carried out at voltages of +0.9 V. [Ot.So.]

926 – Polarometric titration with two indicating electrodes (in Russian). I. S. Savitskaia and O. A. Songina. *Zavodskaya Lab.*, 26 (1960) 282.

A review on polarometric titrimetry, dealing mainly with oxidation–reduction titrations, neutralisation and precipitation reactions. Titration in the presence of organic reagents, instruments and the application of polarometric titrations in practical analyses are also mentioned. 87 literature citations, up to 1958, are listed. [Ot.So.]

927 – Jaroslav Heyrovský: Nobel Laureate. Petr Zuman (Czechoslovak Academy of Science, Prague, Czechoslovakia) and Philip J. Elving (University of Michigan, Ann Arbor, Michigan, U.S.A.). *J. Chem. Educ.*, 37 (1960) 562.

A biography of Heyrovský and his role in the development of polarography. [D.S.Ru.]

928 – Polarography of santonin. Shu-Hao Tian and Tong-Hui Chow. *Acta Pharm. Sinica*, 7 (1959) 17.

Below pH 3.5 santonin gives only one wave, due to a one-electron reversible reduction, whose $E_{1/2}$ shifts towards more negative values as the pH increases; in the wave 3.5–9.0 an additional range (one-electron irreversible reduction) appears, into which the first one merges at pH values above 9.0; the second wave is diffusion-controlled as studies of Hg-height and the influence of the temperature on the limiting current demonstrate. The behaviour of santonic acid is very similar, its $E_{1/2}$ being slightly more negative. Santonic acid is polarographically inactive. Samples of *Artemisia* can be analysed in about 90 min, the results obtained being in good agreement with those given by the gravimetric procedure; the method uses a boric acid–KCl–NaOH buffer of pH 10 containing 25% (v/v) of ethanol and measures the wave-height at –1.7 V(S.C.E.). [Ca.Cas.]

929 – Stoichiometry in the estimation of disulphide in intact proteins using mercuric chloride. S. J. Leach (Division of Protein Research, C.S.I.R.O., Parkville, Melbourne, Victoria, Australia). *Biochim. Biophys. Acta*, 33 (1959) 264.

A method is described in which at pH 9 in the presence of excess sulphite and of 8 M urea, disulphide and mercapto groups in soluble proteins can be titrated with HgCl_2 , the end-point being detected amperometrically by means of the dropping Hg electrode; the correction for thiols is given by a separate polarographic determination.

In insoluble proteins, the titration is carried out by adding an excess of HgCl_2 ; with 8 M urea and at pH 9 the reaction is complete in 18 h. From measurements of the initial, final and blank diffusion currents with the above method, the thiol content is determined at -1.0 V vs. S.C.E. [Ca.Cas.]

930 – Influence of surface-active compounds on the polarographic determination of L-ascorbic acid (in Czech). J. Davidek and J. Manouskova (Central Research Inst. of the Food Industry, Prague, Czechoslovakia). *Průmysl Potravin*, 10 (1959) 96.

In the presence of 1.25% gelatin and 10% dextran slow polarographic measurements are obtained although low results are caused by the presence of surface-active agents; the results are improved by the method of standard additions (add known amounts of an ascorbic acid solution, containing surface-active agents). [Ca.Cas.]

931 – Amperometric titration method for the analysis of mixtures of bismuth, aluminium, calcium and magnesium salts (in Chinese). Yuen-Kai Oong and Hwei-Chen Lee (Dept. of Anal. Chem., Nanking Pharm. College, China). *Acta Pharm. Sinica*, 7 (1959) 99.

Bi^{3+} is titrated at pH 1.5–2 (adjusted with 3 N NaOH and solid chloroacetic acid) with EDTA in the absence of air and in the presence of 0.0025% gelatin, the applied voltage being -0.25 V (S.C.E.); Al^{3+} , Ca^{2+} and Mg^{2+} can be titrated according to the above procedure by treating the solution with excess EDTA, adjusting the pH to 4, heating to nearly boiling, adjusting again to pH 8 (NH_3) and titrating the excess EDTA with 0.05 N $\text{Ca}(\text{NO}_3)_2$, the applied voltage being $+0.05$ V (C.S.E.). Ca^{2+} and Mg^{2+} can also be titrated with EDTA (voltage $+0.02$ V) at pH 10 (adjusted with 6 N HNO_3) if Al and Bi are masked with triethanolamine; by removing Bi^{3+} with H_2S (pH 4) Ca^{2+} can be titrated with EDTA after adjusting the pH to 8 with diluted KOH and addition of Zn^{2+} as indicator, the voltage being -1.6 V and air being excluded. [Ca.Cas.]

932 – Amperometric determination of mercapto groups in grain peteolysis (in Russian). G. I. Kotlyar (Lvov Trade-Economics Institute, U.S.S.R.). *Biokhimiya*, 24 (1959) 15.

The determination was carried out by adding 1 ml of the aqueous extract of the autolysed material (powdered grain after 2 or 4 h; wheat, rye and barley before and after 96 h germination) to 50 ml of alkaline solution (0.2 N NH_3 and 0.2 N NH_3NO_3) with 1 ml of 0.001 N AgNO_3 , the solution being saturated with gaseous nitrogen throughout the operation. Owing to the precipitation of Ag salts of the SH-containing substances, a decrease in the diffusion current was observed at the rotating Pt electrode; the back titration procedure employed avoids any oxidation or chemical combination of the groups to be titrated.

It has been found that the SH-groups content was high after a 4-h autolysis, particularly in the case of the germinated grains. [Ca.Cas.]

933 – Polarographic determination of cobalt, vitamin B2 (riboflavin) and vitamin C (ascorbic acid) mixtures in tablets and ampoules. S. Arizan, M. Popa and M. Sterescu. *Rev. chim. (Bucharest)*, 10 (1959) 109.

Co is initially oxidised in alkaline solution (NH_3) with Na-perborate and then the hexa-aminocobaltic ion determined by polarography: since this procedure destroys both riboflavin and ascorbic acid no interfering substances are present. After extraction (5% Na salicylate) of the sample, riboflavin is also polarographically titratable, while ascorbic acid can be polarographed after dilution with acetic acid–Na acetate buffer (pH 4.6). Conventional reagents do not interfere, and the errors are less than 2%. [Ca.Cas.]

934 – Determination of iodine affinity for starch by amperometric titration. Masaharu Ito and Shigekazu Yoshida (Faculty of Agriculture, Univ. of Agriculture and Technol., Fuchu, Tokyo, Japan). *Bull. Agr. Chem. Soc. Japan*, 23 (1959) 34.

During β -amylolytic processes, the quantity of I_2 combined with the substrate can be followed amperometrically, by means of a rotating Pt electrode and a S.C.E., without application of an external tension. Sharper end-points than in conventional methods are obtained, the only drawback being the variability of the electrode sensitivity. [Ca.Cas.]

935 – Polarographic determination of the cooking degree of pulp. F. Dubšík (Sveročeské Papírny, Štětí, Czechoslovakia). *Papír a celulosa*, 14 (1959) 5.

The excess of KMnO_4 employed for the oxidation of lignin (Künge method) is determined by adding Fe^{2+} and polarographically measuring its excess in citrate buffer; the influence of Mn^{2+} is compensated for by means of a blank. [Ca.Cas.]

936 – Determination of the water content of polyamide shreds using the Karl Fischer reagent by the dead-stop method (in German). G. Glöckner and W. Meyer (VEB Thüringsche Kunstfaser Werk "Wilhelm Pieck", Schwarzta, E. Germany). *Faserforsch. u. Textiltech.*, 10 (1959) 83.

Water is extracted from the sample with anhydrous methanol, and the extract titrated by means of the Karl Fischer reagent, the end-point being detected by methods based on polarisation-current or -voltage. [Ca.Cas.]

937 – Polarographic determination of noradrenaline, adrenaline and aludrine (isoprenaline). E. Romontian, A. Gross and I. Schwartz (Bucharest, Rumania). *Rev. chim. (Bucharest)*, 10 (1959) 111. The sample of the amine sulphate (2 ml) (adrenaline and isoprenaline) or hydrochloride (noradrenaline) is diluted with a basic solution (2 ml) and, after addition of gelatin solution (1%, 3 drops) in order to suppress the maxima, is deaerated by bubbling with H for 5 min and then polarographed (Heyrovský type V 301 apparatus, 4 V, galvanometer sensitivity 1/200, Hg flow rate 1 drop/3 sec).

The authors report figures for $E_{\frac{1}{2}}$ versus S.C.E. obtained with 8 basic solutions, at pH values in the pH range 1.5–9.5. The steps obtained are proportional to the concentration and therefore utilizable for quantitative determinations. [Ca.Cas.]

938 – Electron transfer in reduction processes of hydrocarbons (in English). A. C. Aten (Free University, Amsterdam, The Netherlands). *Thesis*, 1959.

In this thesis the polarographic behaviour of hydrocarbons with conjugated double bonds has been studied in dimethyl formamide solutions. In this medium there are observed two one-electron waves, the first corresponding to the formation of the mono-negative ion, the second one at more negative potentials, corresponding to the formation of the dinegative ion. If the proton activity of the medium is increased by adding water, the second wave is shifted to more positive potentials and becomes irreversible. Qualitative information about the reaction mechanism was obtained from a.c. polarograms. The transfer rates were obtained by plotting R_f and $1/\omega C_f$ (measured by means of an impedance bridge) against $\omega^{-\frac{1}{2}}$. Two parallel straight lines were obtained from the slope of which $D_{\frac{1}{2}}$ is calculated. From the horizontal distance between the lines $D_{\frac{1}{2}}/k$ may be found. By carrying out measurements at various temperatures, the activation enthalpy may be found from $k = k_0 \exp(-[\Delta H^*/RT])$.

The rate constant k is higher for the first step than for the second. For the second step k is relatively high if the reduction tension is less negative than -1.5 V and relatively low if the reduction tension is more negative than -1.5 V (against S.C.E.), whereas the rate constant for the first step is high irrespective of its reduction tension. This indicates that the reduction of anions at fairly negative tensions is inhibited by a change in the double-layer structure. [C.I.Moo.]

939 – Thiourea complexes of some noble metals. A polarographic determination of rhodium. F. Pantani and P. G. Desideri (Inst. Anal. Chemistry, University of Florence, Italy). *Talanta*, 5 (1960) 69.

Rhodium(III) stabilized by heating in thiourea solution, gives a polarographic irreversible wave at about -0.4 V vs. S.C.E., suitable for its determination. The influence of the supporting electrolyte, rhodium and thiourea concentrations, as well as of pH and gelatine are investigated. As supporting electrolyte 0.5 M KCl and as the maximum suppressor gelatine in concentrations not less than 0.002% may be used. Reproducibility is obtained in neutral or slightly acidic media. Because a rhodium complex is involved, the more thiourea there is present, the more the $E_{\frac{1}{2}}$ is shifted to negative values. The limiting current proportional to the rhodium concentration is really a diffusion-controlled one: it is directly proportional to the square root of the height of the mercury column. Platinum interferes, iridium does not, and palladium can be determined simultaneously with rhodium. When rhodium and palladium are present together with an excess of thiourea, an anodic-cathodic wave is produced by palladium and a cathodic wave for rhodium. Evidence is given for the presence of a bi-coordinated platinum complex and mono- and tetra-coordinated palladium complexes. [Ja.Inc.]

See also abstracts nos. 810, 814, 821, 825–827, 831, 840, 849–851, 954, 961, 964, 991.

4. Potentiometry

940 – Determination of chloride ion in glycol by pCl measurement. R. B. LeBlanc and R. T. McFadden (Texas Div., Dow Chemical Co., Freeport, Texas, U.S.A.). *Talanta*, 5 (1960) 78.

Measurement of pCl with a silver-silver chloride electrode affords a rapid means for the determination of chloride in solution above the solubility limit of silver chloride. As comparison electrode S.C.E. can be used. The salt bridge is of potassium nitrate to eliminate any chloride contamination. The Ag-AgCl electrode was prepared as follows. A paste was made of 7 parts of silver oxide, 1 part of silver chlorate and a little water. Platinum spirals were coated with the paste and placed in a furnace at 650° for 7-8 min. The electrode was cooled and was then used as an anode in a 0.2 M HCl solution for 1 h with 2 mA of current flowing. After electrolysis the electrode was soaked in 0.01 M KCl solution for 1-2 days.

A calibration curve was constructed for chloride in glycol. A series of solutions of different chloride concentrations (0-1 p.p.m.) were prepared. Five drops of 3 M KNO₃ were added to 100 ml of each solution and the tension was determined between the Ag-AgCl and S.C.E. electrodes. Glycol samples with unknown chloride concentrations were analysed by the same technique. The chloride concentrations were taken from the calibration curve. The accuracy of the analysis was better than ±0.1 p.p.m. [Ja.Inc.]

941 - The glass electrode as indicator for potentiometric titrations in non-aqueous solutions (in German). H. Frind and A. Busch. *Chem.-Ztg., Chem. App.*, 17 (1960) 568.

The use of glass electrodes as indicators for potentiometric titrations in non-aqueous solutions is described. A vast literature on the titration of various substances in solvents (such as acetic acid, dioxan, ethyl alcohol, acetic nitrile) is reported. [Di.Ciò.]

942 - Clinical biochemistry. E. J. King (Professor of Biochemistry, British Postgraduate Medical School). *Lab. Practice*, 9 (1960) 664.

An apparatus for potentiometric titration of chloride is described. The sample (plasma, serum, etc.) is diluted with dilute nitric acid in a small beaker fitted with continuous magnetic stirring. A special burette with a sealed-in platinum electrode dips into the solution and delivers standard silver nitrate solution. Precipitation of silver chloride occurs until the end-point is reached. The electrical tension between the platinum electrode dipping into the sample is continuously measured. Titration is stopped when the tension reaches a predetermined value corresponding to exact equivalence between the silver nitrate and chloride in the beaker; this tension is established beforehand by blank titration against a measured volume of standard chloride solution. [Di.Ciò.]

943 - The interaction of bis(ethylenediamine)-palladium(II) iodide with potassium and potassium amide in liquid ammonia. George W. Watt and Richard Layton (Dept. of Chemistry, University of Texas, Austin, Texas, U.S.A.). *J. Am. Chem. Soc.*, 82 (1960) 4465.

Die Reaktion von Bis(äthylendiamin)-Palladium(II)-Jodid mit Kaliumamid in flüssigen Ammoniak bei -33.5° wurde mit Hilfe potentiometrischer Titrations untersucht. Es entstehen die Komplexe [Pd(en)(en-H)]J und [Pd(en-H)₂]. Aus den Reaktionen dieser beiden Verbindungen mit Wasser, verdünnten Säuren und Kaliumtetrajodomercurat(II) ergibt sich, dass [Pd(en)(en-H)]J nur schwach basische Eigenschaften, [Pd(en-H)₂] dagegen stark basische Eigenschaften besitzt. Die Reduktion beider Stoffe in flüssigen NH₃ mit Kalium führt zur Ausscheidung von metallischen Palladium. [Ha.Re.]

944 - Chelate stabilities of certain oxine-type compounds. I. T. J. Lane, A. Sam and A. J. Kandathil (Dept. of Chemistry, University of Notre Dame, Ind., U.S.A.). *J. Am. Chem. Soc.*, 82 (1960) 4462.

Die Säuredissoziationskonstanten von 4-Hydroxybenzimidazol, 4-Hydroxy-2-methylbenzimidazol, 4-Hydroxy-2-äthylbenzimidazol, 4-Hydroxy-bezoxazol und 4-Hydroxy-2-methylbenzoxazol, sowie die Stabilitätskonstanten der entsprechenden Cu(II)-, Pb(II)-, Cd(II)-, Zn(II)-, Ni(II)- und Co(II)-Komplexe werden durch potentiometrische Titrations in 50%-igen Dioxan-Wasser-Mischungen bei 25° bestimmt. Die Benzimidazolkomplexe erweisen sich als beständiger als die entsprechenden Benzoxazolkomplexe. Die erhaltenen Konstanten nehmen in der Reihe Cu > Pb > Cd > Zn > Ni > Co ab. Alle untersuchten Komplexe weisen eine geringere Stabilität auf, als die 8-Hydroxychinolin- und 2(o-Hydroxyphenyl)-benzimidazolkomplexe mit den gleichen Kationen. Diese Erscheinungen werden in Zusammenhang mit den Strukturbesonderheiten der Komplexbildner diskutiert. [Ha.Re.]

945 - Oxidation potentials of arylferrocenes. John G. Mason and Myron Rosenblum (Dept. of Chemistry, Illinois Institute of Technology and Brandeis University, Waltham, Mass., U.S.A.). *J. Am. Chem. Soc.*, 82 (1960) 4206.

Die formalen Oxydationsspannungen von *para* substituierten Phenylferrocenen wurden in wässriger Essigsäure durch potentiometrische Titration bestimmt. Die Oxydationsspannungen der Phenylferrocene zeigen die lineare Abhängigkeit von der Hammett'schen σ -Konstante für die *para* Substituenten. Für die Reaktionskonstante wird ein Wert von -2.41 angegeben. [Ha.Re.]

946 – The acidity and complexes of peroxydiphosphoric acid. Marvin M. Crutchfield and John O. Edwards (Metcalf Chemical Laboratories, Brown University, Providence, Rhode Island, U.S.A.). *J. Am. Chem. Soc.*, 82 (1960) 3533.

Die dritte und vierte Säuredissoziationskonstante K_3 und K_4 von Peroxydiphosphorsäure wurde bei 25° mit Hilfe der pH-Titration des Tetramethylammoniumsalzes mit HCl, bei verschiedenen Ionenstärken der Lösung, gemessen. Die Extrapolation auf unendliche Verdünnung führt zu den Konstanten $K_3 = 6.6 \pm 0.3 \cdot 10^{-6}$ und $K_4 = 2.1 \pm 0.1 \cdot 10^{-8}$. Die Werte für die erste und zweite Dissoziationskonstante, konnten nur aus Analogieschlüssen abgeschätzt werden. Für K_1 wird ≈ 2 und für $K_2 \approx 3 \cdot 10^{-1}$ angegeben.

Komplexbildungskonstanten von Metallkomplexen mit Peroxydiphosphorsäure wurden für die Kationen Li^+ , Na^+ , K^+ und Mg^{2+} bei 25° und der Ionenstärke 1 gemessen. Die Konstanten stimmen mit den entsprechenden Werten der Phosphorsäure überein. [Ha.Re.]

947 – Metal chelates of alkanol-substituted amines. James L. Hall, Warren E. Dean and Edward A. Pacofsky (Dept. of Chemistry, West Virginia University, Morgantown, W.Va., U.S.A.). *J. Am. Chem. Soc.*, 82 (1960) 3303.

Eine potentiometrische Untersuchung der Cu(II)-, Ni(II)-, Co(II)-, Cd(II)- und Zn(II)-Chelate von verschiedenen Alkanol-substituierten Äthylendiaminen wird beschrieben. Von den mono- und disubstituierten Aminen werden sowohl 1 : 1 wie auch 1 : 2 Komplexe gebildet. Erstere lagern sich unter Einfluss von starken Alkali in 1 : 2 Komplexe um, oder bilden ungeladene Chelatverbindungen. Die tetraalkanolsubstituierten Amine können nur 1 : 1 Komplexe bilden. Amine mit 2-Hydroxypropyl-Substituenten erzeugen im Gegensatz zu 2-Hydroxyläthylaminen die stabileren Komplexe. Die Konstanten K_1 und K_2 , sowie der pH-Wert, bei dem die Fällung eines Komplexes einsetzt, sind tabelliert. [Ha.Re.]

948 – The determination of carboxyl groups in polyethylene terephthalate. M. J. Maurice and F. Huizinga (Central Analytical Laboratory N.V., Research Institute (A.K.U. and affiliated companies), Arnhem, The Netherlands). *Anal. Chim. Acta*, 22 (1960) 363.

Three methods for the determination of carboxyl groups in polyethylene terephthalate are investigated, viz. (a) dissolution in hot benzyl alcohol, addition of chloroform, and titration with benzyl alcoholic potassium hydroxide solution to the phenol-red end-point, (b) dissolution in a mixture of *o*-cresol and chloroform, and potentiometric titration with ethanolic potassium hydroxide solution, and (c) dissolution in a mixture of *o*-cresol, chloroform and acetone, and titration with ethanolic potassium hydroxide solution with HF indication of the end-point.

The three methods yield the same results when applied to several samples of different carboxyl content. For several reasons the potentiometric method is preferable to the other two methods [P.Me.]

949 – Stability of copper biguanide complexes (in English). Asit Kumar Ray (Dept. of Inorganic Chemistry, Jadavpur University, Calcutta, India). *Z. anorg. u. allgem. Chem.*, 305 (1960) 207. The successive stability constants of some copper biguanide complexes have been determined by potentiometric measurements. The dependence of chelate stability upon the basic strength of the ligands is discussed. The biguanide molecule usually behaves as a base resembling ammonia, combining with protons to form a conjugated acid similar to the NH_4^+ ion. However, it can also act as a potential acid by donating a proton thus behaving as an ampholyte. In the latter case it gives rise to a polar ion; in this polar form it combines with metal ions to generate metallic complexes of the third order.

It was considered here whether the metal ion functions in a manner analogous to the hydrogen ion, and it may be reasonably concluded, from experimental and theoretical results, that one of the components of the forces responsible for holding the metal in the complex has the same character for both metal and hydrogen. [Di.Ciò.]

950 – Potentiometric titration of bismuth with sodium and lithium ferrocyanide (in Polish). H. Basińska and Z. Orylski (Dept. of Inorganic Chemistry, University of Warsaw, Poland). *Chemia Analityczna*, 5 (1960) 187.

During potentiometric titrations of bismuth with sodium and lithium ferrocyanide it was found that the $\text{Bi} : \text{Fe}(\text{CN})_6^{4-}$ ratio in the precipitate equals 1.472, which approximately corresponds to the formula $5 \text{Bi}_4[\text{Fe}(\text{CN})_6]_3 \cdot 2 \text{Bi}(\text{NO}_3)_3$. In this titration approx. 0.1 M solutions were used; a platinum electrode was used as the indicator electrode with a saturated calomel electrode as the comparison electrode. Compared with gravimetric determinations of Bi as BiOI the error is less than 1%. Addition of ethanol did not improve the results. [Ad.Hu.]

951 – Détermination électrométrique du pH (en Anglais). R. Bates (National Bureau of Standards, Washington, D.C., U.S.A.). *Chimia*, 14 (1960) 111.

L'auteur donne un aperçu très suggestif du difficile problème de la détermination du pH. Il

montre comment cette méthode s'est développée, comment l'échelle des pH a été établie; déterminés en tenant compte des coefficients d'activité et donne des courbes concernant les variations du pH selon le coefficient d'activité de l'ion chlore. Un tableau est présenté, qui donne une liste des standards N.B.S. avec leurs propriétés et leurs variations en fonction de la température. Il traite aussi de l'épineux problème de la standardisation en milieu alcalin et ce jusqu'au pH 12.45. Le problème de l'échelle internationale est aussi évoqué ainsi que celui, non moins délicat, de son interprétation.

Dans un second chapitre, l'auteur aborde l'instrumentation, un important paragraphe est consacré à l'électrode de verre, avec graphiques et photos, un autre aux électrodes de référence et au pH-mètre du commerce et leurs principales caractéristiques. Vient ensuite un exposé sur la titration automatique et un autre sur le contrôle industriel du pH; l'article se termine sur la bibliographie qui comprend 45 références. Article fort bien fait et qui donne une idée très précise de l'état de la question. [De.Mo.]

952 – Dérivés de la pyridine comme complexants. II (en Allemand). G. Anderegg (Chimie inorganique de l'E.P.F., Zürich, Suisse). *Helv. Chim. Acta*, 43 (1960) 1530.

La formation des complexes du fer bivalent avec les anions de l'acide picolinique et dipicolinique a été décrite dans une publication précédente. Le comportement du fer trivalent a été étudié ici à l'aide des tensions d'oxydo-réduction Fe(III)/Fe(II) mesurés en présence d'un grand excès de complexant organique.

De nombreux essais ont été faits soit à pH et $(\text{Fe(III)})_t$ total constants, soit en faisant varier ces 2 facteurs.

L'acide dipicolinique forme simplement les complexes Fe(Dipic)^+ et Fe(Dipic)^{2-} et ceci déjà à des valeurs de pH très faibles.

Le comportement du fer avec l'acide monopicolinique est différent. Malgré la nature "bidentate" de ce complexant, seuls les complexes 1 : 1 et 1 : 2 sont formés avec le Fe(III). Le complexe 1 : 2 donne déjà au-dessous du pH 3 le $\text{Fe(Pic)}_2\text{OH}$ et son dimère $\text{Fe}_2(\text{Pic})_4(\text{OH})_2$ si $(\text{Fe(III)})_t$ est supérieure à 10^{-4} . L'absorption optique de ce dimère est très semblable à celle de $\text{Fe}_2(\text{OH})_2^{4+}$, ce qui suggère une structure analogue.

La méthode décrite pour expliquer l'équilibre entre les complexes monomères, dimères et polymères doit être d'application générale. [De.Mo.]

953 – Potentiometric determination of mercury(II) with ethylenediamine tetraacetic acid: analysis of binary mixtures. H. Khalifa and M. G. Allam (Anal. Chem. Dept., Faculty of Science, Cairo University, Giza, Egypt). *Anal. Chim. Acta*, 22 (1960) 421.

Potentiometric determination of mercury(II) with EDTA, using silver amalgam as the indicator electrode, is suitable for 200 μg to 100 mg of mercury. A procedure reported for the analysis of binary mixtures of mercury and barium is based on the use of selective pH. Binary mixtures of mercury and aluminium were analysed with the aid of masking agents such as triethanolamine or ammonium fluoride. Binary mixtures of mercury with any of the other cations mentioned were analysed by two potentiometric titrations; one gave the content of mercury and the other the content of mercury plus the other metal. In all cases the error is less than 1%. [P.Me.]

954 – Reducing properties of cerous ion in alkaline media. N. H. Furman and A. J. Fenton, Jr. (Princeton University, Princeton, N.J., U.S.A.). *Anal. Chem.*, 32 (1960) 745.

The stoichiometric reactions of ferricyanide and permanganate with cerous ion in strong carbonate solutions are investigated. An indirect method for determining glucose is elaborated. The most suitable method for end-point detection depends on the concentration of the titrant. Potentiometric end-point detection is accurate over the whole concentration range studied. Amperometric titrations made with either one or two polarized electrodes were equally effective. The end-point is sharp even with 0.0005 *N* cerous solutions. [Kl.Gr.]

955 – Influence of metal ions and sample acidity on determination of manganese. W. G. Scribner (Research Eng. Div., Monsanto Chem. Co., Dayton, Ohio, U.S.A.). *Anal. Chem.*, 32 (1960) 966.

The methods of Lingane and Karplus for the potentiometric titration of manganese(II) with permanganate in a neutral phosphate medium has been closely examined for the influence of certain metal ions. Low results for the titration of Mn are obtained if the acidity of the solution is high and if copper, iron and cobalt are present. Oxidation of some of the manganese ions occurs in solutions containing Mn or Mn in combination with Zn, Cd, Mg or Al. Oxygen is reduced to hydrogen peroxide which is titrated with permanganate. The net titration then gives accurate results for Mn. Indication of the titration procedure is made potentiometrically. [Kl.Gr.]

956 – Simple method for the estimation of standard oxidation potentials and for controlling their uniformity on the basis of the Luther–Wilson rule. L. S. Csányi (Institute of Inorganic Chemistry, University of Szeged, Hungary). *Magyar Kém. Folyóirat*, 65 (1959) 415.

It has been proved that the Luther–Wilson rule can be written in the form $E_i^\circ = f(\Sigma n_i)$, E_i° being the standard oxidation tension of the corresponding couples and Σn_i the sum of the oxidation number of the species involved in them. This function can be applied for the estimation of unknown standard oxidation tensions and for controlling their uniformity. The oxidation tensions of the couples Cr^{3+} – Cr^{4+} and Cr^{4+} – Cr^{5+} were given as 2.104 V and 1.34 V, respectively. [E.Juh.]

957 – The theory of the alkaline error of the glass electrode. Ch. Oláh (Institute of Physical Chemistry, Technical University, Budapest, Hungary). *Periodica Polytech.*, 4 (1960) 141.

The glass electrode in an acid medium has been considered as a simple hydrogen electrode, and in an alkaline medium as a hydrogen–alkali mixture electrode. Its behaviour can be characterized by the equilibrium constant of the hydrogen–alkali ion exchange (K):

$$\Delta \varepsilon = \frac{RT}{F} \ln \left(1 + K \frac{a_K}{a_H} \right).$$

The theory has been further developed to consider the possibility that the anions of the silicate lattice may be in dissociation equilibrium with the hydrogen or alkali ions of the glass. Considering this effect, a more general equation for the alkaline error has been derived, by which an explanation may be given for different phenomena; this equation resembles the simple formula for mixture electrodes.

The alkaline error is:

$$\Delta \varepsilon = \frac{1}{2} \frac{RT}{F} \ln \left[\left(1 + K \frac{a_K}{a_H} \right) \left(1 + K \frac{K_H}{K_K} \cdot \frac{a_K}{a_H} \right) \right]$$

where K_H and K_K are the dissociation constants of the silicate anions of the glass and a_H and a_K the activities of the hydrogen and alkali ions, respectively. [E.Juh.]

958 – The first hydrolysis constant of the Ni^{2+} ion (in Italian). F. Achenza (Institute of General Chemistry of Cagliari, Italy). *Ann. chim. (Rome)*, 49 (1959) 624.

Potentiometric measurements have been carried out with a glass electrode on $\text{Ni}(\text{NO}_3)_2$ solutions, using slightly alkaline 10^{-2} M K_2SO_4 or KClO_4 as the titrant. A mathematical treatment of the experimental data shows that a plot of $p(a_H +^2 - K_w + c_{\text{Na}^+} a_H + f)$ versus $p c_{\text{M}}'$ is a straight line with a slope of 1. The intercept when $p c_{\text{M}}' = 0$ yields the value of pK_1 , which is shown to be 10.92 at 25°. [Fr.Pan.]

959 – Potentiometric and etometric titrations of thioacetamide with AgNO_3 (in Italian). E. Bova-lini and M. Piazzi (Chem. Laboratory, Naval Academy, Leghorn, Italy). *Ann. chim. (Rome)*, 49 (1959) 1067.

Thioacetamide solutions with concentrations as low as 0.001 M can be titrated potentiometrically with silver nitrate in ammonia solutions, optimum pH being 8.5–9. A glass electrode and a silver–silver sulphide electrode appeared to be suitable. The same titrations can be performed with more accuracy etometrically in accordance with the method of Bobtelsky. In this way silver can be determined in the range 0.05–1 mg. The silver–thioacetamide mole ratio is 1:1. [Fr.Pan.]

960 – The potentials of the mercurous sulphate/mercury electrode. W. H. Beck, J. V. Dobson and W. F. K. Wynne-Jones (Dept. of Chem., King's College, Newcastle-upon-Tyne, Great Britain). *Trans. Faraday Soc.*, 56 (1960) 1172.

The tension of the cell: $\text{Pt}/\text{Hg}/\text{Hg}_2\text{SO}_4/\text{H}_2\text{SO}_4(M)/\text{H}_2$ -Pt has been measured over the temperature range 5–55° and sulphuric acid concentration range 0.1–8 M. Using the activity coefficient values deduced from vapour pressure data, U_0 values can be calculated. The results obtained were compared with the corresponding values calculated from Hamer's observations in the same way. The results obtained are found to agree satisfactorily with the vapour pressure data on the activities of sulphuric acid and with the calorimetric data on the partial molal heat content of the acid. [M.K.Hus.]

961 – Complex formation in solutions of copper oxalate. A. McAuley and G. H. Nancollas (Chem. Dept., University of Glasgow, Great Britain). *Trans. Faraday Soc.*, 56 (1960) 1165.

Owing to the extremely small solubility of copper oxalate ($1.6 \cdot 10^{-4}$ M at 18°), the identification of complex species present in its solution is rather difficult. Potentiometric measurements at a constant ionic strength of 0.1 M were thus used to try to identify and determine the stabilities of the complex species present in solutions of copper oxalate over as wide a range of concentration as possible. Measurements at low concentrations yielded the thermodynamic association constants. Polarographic measurements of higher oxalate concentrations were also made and found to support the potentiometric values. [M.K.Hus.]

962 – Interpretation of potentiometric titration of H-montmorillonite. A. M. Pommer and D. Garroll (U.S. Geological Survey, Washington, D.C., U.S.A.). *Nature*, 185 (1960) 595.

It was observed that the pH titration curves of hydrogen clays with strong monovalent bases have various characteristics such as variation in steepness of the slope of different parts of the curve, variations of the kind of clay mineral, amount of mineral in suspension and the cations used to produce neutralisation.

Samples of montmorillonite are converted to the hydrogen form according to the method of Aldrich and Buchanan. No aluminium is found to exist in the exchange positions. Additions of increasing increments of 0.1 N NaOH to a constant volume of the material are made and the pH values are repeatedly measured till they give constant values. Plots of ml of NaOH against pH are made. When the pH values are plotted against $\log V$ (volume of base added), straight lines are usually obtained. [M.K.Hus.]

963 – Determination of sodium ions in acidic silica sol systems. Th. A. Thauli (Research Dept., Inorg. Chem. Div., Monsanto Chemical Co., St. Louis, Mo., U.S.A.). *Anal. Chem.*, 32 (1960) 186. A new tension-measurement method for the determination of sodium in acidic silica sol is described. A 10 g portion of the sample in 40 ml of water is passed through a prepared Dowex 1 column (20 to 50 mesh) and washed to give at least 230 ml of effluent which is contained in a 250 ml volumetric flask. The pH is adjusted to 6.0 ± 0.2 with sulfuric acid and then the solution is made up to the mark with water. The millivolt potential of the solution is determined with a Beckman Zeromatic pH-meter Model 9600. The 3500 ohm resistor is changed to a 700 ohm one to allow measurement of sodium ions from 0 to 1000 p.p.m. An indicator cationic electrode No. 78137 V and a Beckman calomel comparison electrode are used. The equation for the calculation of the sodium content is: $S = 0.0203 \text{ Potential} + 2.914 \text{ at } 26 \pm 1^\circ$. The standard deviation is 5.7%. [Kl.Gr.]

964 – Quelques méthodes employées dans un laboratoire industriel pour la détermination du groupe NH_2 aromatique. R. Goupil (Service analytique du laboratoire central de la compagnie Française des matières colorantes). *Chim. anal.*, 42 (1960) 300.

L'auteur passe en revue un assez grand nombre de méthodes utilisées dans les laboratoires industriels pour l'identification et le dosage du groupe NH_2 dans les amines aromatiques parmi lesquelles la méthode potentiométrique et la méthode "Dead Stop" à l'aide d'une solution standard de nitrite de soude. Dans le titrage direct l'apparition de l'excès d'acide nitreux est mis en évidence par une potentiométrie à deux électrodes de platine indicatrices (10×15 mm) parcourus par un courant non précisé. La base à doser est $1 \text{ à } 2 \cdot 10^{-2} M$. L'auteur dose ainsi l'aniline, l'acide sulfamilique, les toluidines-2 et 4, la chloraniline-4, la dichloro-2,5 aniline, la méthoxy-2, diéthyl-5 sulfamido aniline, la nitro-3 aniline, la benzidine, la dianisidine et la tolidine. Les corps suivants: l' amino-4 azo benzène et le diamino-4,4' disulfo-2,2' stilbène nécessitent un dosage en retour par la paranitraniline ou la paratoluidine. [Bad.Lam.]

965 – L'acidimétrie en milieu non aqueux. I. Base de la méthode. J.A. Gautier II. Descriptions des techniques et applications. F. Pellerin (Faculté de Pharmacie, Paris, France). *Bull. soc. chim. France*, (1959) 279, 283.

Il s'agit d'une mise au point destinée à renseigner les analystes sur le dosage des polarités acide et basique en milieu non aqueux. L'auteur rappelle les théories d'Arrhénius, de Broensted et de Lewis. Il aborde ensuite l'influence du solvant sur la force d'un couple acide-base en étudiant successivement l'effet dissolvant, l'effet diélectrique, l'effet prototropique. Selon leur nature les solvants sont amphiprotiques, aprotiques ou bien seulement acide ou seulement basique.

On propose ensuite des renseignements pratiques sur le dosage des bases, de leur mélange et sur celui des acides. L'emploi d'indicateurs colorés et de méthodes électrochimiques indicatrices est abordé. On cite quelques exemples de dosage dans le diméthylformamide: 42 références.

[Bad.Lam.]

966 – Acid-base titrations with the tellurium electrode. John A. Ricketts and Ronald E. Bowen (De Pauw University, Greencastle, Indiana, U.S.A.) *J. Chem. Educ.*, 37 (1960) 473.

The reversible oxidation tension of the tellurium-tellurium oxide electrode is shown to be a linear function of pH. The results from titrations of hydrochloric and acetic acid are compared using both the tellurium and glass electrodes. Approximately two minutes is required for the tellurium electrode to come to equilibrium after each addition of acid or base. The preparation of the plated tellurium electrode is given. [D.S.Ru.]

967 – The electrochemical behaviour of the nickel oxide electrode. II. Quasi-equilibrium behaviour. P. L. Bourgault and B. E. Conway (Dept. of Chemistry, University of Ottawa, Canada). *Can. J. Chem.*, 38 (1960) 1557.

The electrode tension of the nickel oxide electrode has been determined as a function of water and solute activity in aqueous solutions of potassium hydroxide. The electrode which was charged to a mean state of oxidation corresponding to 50% Ni(II) and 50% Ni(III), was examined after long periods of time by cathodic and anodic tension decay measurements after polarisation to establish the quasi-reversible tensions by the two methods. The results are discussed in terms of stoichiometry of the tension-determining reaction. [D.S.Ru.]

968 – Determination of chlorine in bleached shellac. O. Tweet, W. K. Miller and R. H. Simon (S.C. Johnson & Sons Inc., Racine, Wis., U.S.A.). *Soap Chem. Specialities*, 35 (1959) 95.

After discussing the unreliability of various methods for the determination of Cl in bleached shellac, the following procedure is recommended: Cl⁻ is determined by dissolving a 1 g sample in *n*-butanol, extracting with water and titrating potentiometrically with 0.02 *N* AgNO₃ after acidification with HNO₃, whereas the total Cl is determined by dissolving the sample in isopropanol, refluxing in the presence of metallic Na (2.5 g Na), diluting with water, acidifying with HNO₃, adding excess AgNO₃ and titrating the excess reagent with 0.1 *N* KCNS. A more accurate method for the total Cl involves the decomposition of 0.3 g of the sample in a Parr bomb; the sample is then dissolved in water, and the resulting Cl⁻ titrated as above. [Ca.Cas.]

969 – Rapid simultaneous potentiometric determination of chromium, vanadium and iron in carbides by means of titanium(III) chloride. O. Dufek and H. Tuma (S.V.U.M.T., Prague, Czechoslovakia). *Hutnické Listy*, 14 (1959) 246.

A 10–15 mg sample of the carbide is dissolved in 3–5 ml of 60% HClO₄, several drops of conc. HNO₃ are added and the solution evaporated. After 30 min several drops of water and 15 ml concentrated HCl are added, and the resulting solution titrated potentiometrically with TiCl₃ in a stream of CO₂; an apparatus consisting of Pt and S.C.E. electrodes (galvanometer provided with an adapter for derivative measurements and sensitivity control) is used.

The tension changes observed are respectively due to: (i) reduction of Cr(VI) to Cr(III) together with V(V) to V(IV); (ii) of Fe(III) to Fe(II); (iii) of Mo(VI) to Mo(V).

At this point, 40 ml of 40% Na-citrate are added and the titration resumed in order to observe the tension change corresponding to the reduction of V(IV) to V(III). By subtraction of the titrant volume consumed in the last operation from the titrant volume consumed in the first operation the Cr can be calculated. [Ca.Cas.]

970 – Potentiometric determination of high molecular fatty acids and fatty acid mixtures. C. Sass (REWO Chem. Fabrik G.m.b.H., Schlüchtern, Deutschland). *Fette u. Seifen*, 61 (1959) 93.

Typical, reproducible and accurate (1–3%) curves are obtained when suitable solutions of the potassium salts (obtained by dissolving a 0.12–0.25 g sample in 5 ml of dioxane, titrating against phenolphthalein with 0.5 *N* alcoholic KOH, and diluting to 250 ml with water) are potentiometrically titrated with 0.1 *N* AgNO₃ in the presence of a calomel electrode. Additions must be done in 0.25 ml aliquots, and the titration time is increased by the presence of unsaturated acids (not more than 25% oleic acid in the sample is measurable). Unknown components may be identified by observing the effect of the additions of known samples on the titration curve. [Ca.Cas.]

971 – The determination of plutonium based on National Bureau of Standards potassium dichromate. C. E. Pietri and J. A. Baglio (U.S. Atomic Energy Commission, New Brunswick Lab., N.J., U.S.A.). *Talanta*, 6 (1960) 159.

A new laboratory, using glove boxes of improved design, has been built to study the chemistry of plutonium, to develop methods of analysis and to prepare plutonium compounds for standards. In the method for the determination of plutonium developed at this laboratory, high purity (99.96%) plutonium metal was dissolved in 4 *N* H₂SO₄, reduced to Pu(III) with zinc amalgam in a Jones reductor and titrated to Pu(IV) with standard K₂Cr₂O₇. Polarized gold electrodes were used to indicate the end-point. A relative standard deviation of 0.04% has been obtained for 70–141 mg samples. The average results were within 0.01% of the purity of the plutonium metal as determined by spectrographic analysis. The advantages of the primary standard K₂Cr₂O₇ over Ce(SO₄)₂ as used in other methods are discussed as well as the detection of the end-point by polarized electrodes *vs.* the comparison–indicator electrode system. [Ja.Inc.]

972 – Potentiometric examination of some precipitation and complex reactions of silver in strongly alkaline medium. Gh. Facsko and R. Minges (Lab. Electrochem., Polytechn. Inst., Timisoara, Rumania). *Talanta*, 5 (1960) 102.

The potentiometric titration of silver using silver and saturated calomel electrodes in strongly alkaline solutions of 4-sulphamidobenzoic acid was investigated. As titrants potassium chloride, bromide, iodide and cyanide were used. The tension change is very sharp and the amounts reacting nearly stoichiometric in the case of iodide or cyanide.

The separation of silver by means of 4-sulphoamidobenzoic acid in alkaline or carbonate-containing media, followed by a potentiometric titration with potassium cyanide or iodide promises a rapid method for the determination of silver. [Ja.Inc.]

973 – New redox systems. III. Indirect cerimetric determination of cobalt. F. Vydra and R. Pribil (Lab. Anal. Chem., Czechoslovak Academy Science, Prague, Czechoslovakia). *Talanta*, 5 (1960) 92. The previously studied redox reaction (*Talanta*, 5 (1960) 44):

$$[\text{Fe}_2(\text{Phen})_4(\text{OH})_2]^{4+} + 2 \text{Co}(\text{Phen})_3^{2+} + 2 \text{HPhen}^+ \rightleftharpoons 2 \text{Fe}(\text{Phen})_3^{3+} + 2 \text{H}_2\text{O}$$

is utilised for the indirect cerimetric determination of cobalt. The determination is based on the titration of the resulting ferroin with a potentiometric or visual end-point. 3 mg of cobalt could be reliably determined in the presence of 90 mg of iron, 110 mg of Ni, 25 mg of Cd, 65 mg of Zn, 20 mg of Cu, 30 mg of Mo, 45 mg of VO_3 and 50 mg of W. Alkaline earths, rare earths, Th, Be, Ti, U, Cr, Al, Pb and Zr do not interfere. The method is applicable for the determination of cobalt in ferrous alloys (containing 2–40% Co).

Procedure: Treat 0.5 g of the sample with aqua regia, evaporate and dilute. Filter and wash with hot dilute HCl. Dilute the filtrate to 250 ml. Neutralise 25 ml of this solution with 5% NaOH, dissolve the precipitate in the minimum amount of HCl. Adjust the pH to 2–4, and add 10 ml of 0.1 M 1:10-phenanthroline of pH 3. After 15 min acidify the solution with 50 ml of 9 N sulphuric acid, dilute to 200 ml and titrate with 0.05–0.1 M cerium(IV) sulphate solution with potentiometric control, using platinum and saturated calomel electrodes. [Ja.Inc.]

974 – The hydrolysis of copper(II) ion. D. D. Perrin (The Australian National University, Canberra, Australia). *J. Chem. Soc.*, (1960) 3189.

It has been deduced from pH titrations that mononuclear complexes such as CuOH^+ are not present in appreciable amounts, but that the formation of polynuclear complexes of the type $\text{Cu}_n(\text{OH})_{2n-2+2}$ prevails. The acid dissociation constant for $\text{Cu}_2(\text{OH})_2^{2+}$ has been determined as a function of the temperature and the ionic strength (order of magnitude for the log: –10.7). For $\text{Cu}_3(\text{OH})_4^{2+}$ at 20°, $\log \beta_{34}$ is of the order of –22.

pH titration curves using alkali are satisfactorily explained with the assumption that the formation constant is the same for the successive addition of each $\text{Cu}(\text{OH})_2$ "link", for all complexes larger than $\text{Cu}_2(\text{OH})_2^{2+}$. [L.Gi.]

975 – The reduction of V(V) by hydrogen peroxide in solutions of strong acids. G. Kakabadse and H. J. Wilson (Manchester College of Science and Technol., Manchester, Great Britain). *J. Chem. Soc.*, (1960) 2475.

As shown by potentiometric and spectrophotometric measurements, the mechanism of this reduction is rather complex, and appears to consist in rapid peroxidation followed by relatively slow reduction, involving pale yellow vanadyl(V), red-brown monoperoxyvanadyl(V), yellow diperoxyorthovanadate, and blue vanadyl(IV). [L.Gi.]

976 – Indium phosphates: phase-diagram, ion-exchange and pH titration studies. G. E. A. Brownlow, J. E. Salmon and J. C. Wall (Battersea College of Technol., London, Great Britain). *J. Chem. Soc.*, (1960) 2452.

pH titration studies and ion-exchange experiments (using Zeo-Karb 225) indicate that, in the range of pH 0.05–1.25, the extent of complex formation between In^{3+} and the anions decreases in the sequence $\text{HF} > \text{H}_3\text{PO}_4 > \text{HCl} > \text{H}_2\text{SO}_4 > \text{HNO}_3 > \text{HClO}_4$. As shown by ion-exchange experiments, anionic and cationic phosphate complexes can be formed under specified conditions. [L.Gi.]

See also abstracts nos. 818, 821, 823, 833-837, 845, 846, 1056, 1057, 1059, 1061.

5. Conductometry

977 – Conductivity of aqueous sodium stannate solution. P. T. Good (Admiralty Materials Laboratory, Holton Heath, Dorset, Great Britain). *Nature*, 185 (1960) 840.

When sodium stannate prepared by Zocher's method is dissolved in water at 25°, the pH shows a remarkable increase and the steady state is reached after about one week. The change of conductivity within this period was followed using an electrodeless capacity-coupled cell. A regular

increase in the conductivity with time was observed till a limiting value was attained after seven days. Specific and equivalent conductivities at zero time are elucidated through extrapolation, while the equivalent conductivity at infinite dilution was obtained from a Kohlrausch plot. The increase in the conductivity is mainly due to the increase in $[\text{OH}^-]$ in solution. [M.K.Hus.]

978 – The transference number of phosphoric acid by the moving boundary method. M. Kerker, H. E. Bowman and E. Matijevec (Clarkson College of Technology, Potsdam, New York, U.S.A.). *Trans. Faraday Soc.*, 56 (1960) 1039.

The moving boundary method was applied for measuring the hydrogen-ion transference number of H_3PO_4 and a comparison with the corresponding values obtained with the tension method was made. It was found that the new value was appreciably lower and lead to an equivalent conductance for the H_2PO_4^- ion, which was in better agreement with values determined from conductance data. With phosphoric acid, the ratio of conductance of the solvent to solution was determined by using a Leeds and Northrup type LC conductivity cell with 100 cycle equipment. The cation transference number of phosphoric acid was evaluated over a wide concentration range. Sharp boundaries were not available at concentrations higher than 0.044 M , whereas at concentrations lower than 0.0088 M the precision of the results became poorer. [M.K.Hus.]

979 – Ionic conductivity in concentrated cells. J. Arotzky and M. C. R. Symons (Dept. of Chem., University of Southampton, Great Britain). *Trans. Faraday Soc.*, 56 (1960) 1426.

The effect of solutes added upon the conductivity of oleum in the region of 65% is studied in order to find out whether the general behaviour is comparable with that of solutions in sulphuric acid, and if so to test the usefulness of this technique in studying solutions of oleum. It is found that 65% behaves in a manner closely analogous to that in sulphuric acid. The results are explained in terms of the postulate that the main conductor is the characteristic anion of the medium, probably hydrogen pyrosulphate, HS_2O_7^- . Boron trichloride reacts to give a non-conducting compound, which is thought to be $\text{B}(\text{HS}_2\text{O}_7)_3$, and this reacts with HS_2O_7^- ions to yield $\text{B}(\text{HS}_2\text{O}_7)_4^-$, a compound which contributes little to the total conductivity. This substantiates a method for determining the concentration of HS_2O_7^- ion in solution. Plots of conductivity against concentration in the range 10^{-2} – 10^{-1} M are accurately linear. [M.K.Hus.]

980 – Methods of conductivity measurements (in German). H. Wirth (Inst. Entw. chem.-phys. Analysenmeth., Weilheim/Obb., Germany). *Mitt. Inst. Entw. chem.-phys. Analysenmeth.*, 3 (1960) 51.

Ausgang der Betrachtungen von der Brückenmethode als genauestem Verfahren zur Messung von Widerständen und Leitfähigkeiten. Die sehr verbreitete Wheatstone-Brücke mit der Bestimmungsgleichung für den unbekanntenen Widerstand $R_x = (R_2R_3)/R_1$ kommt in zwei verschiedenen Schaltungen zur Anwendung:

(1) R_1 und R_2 sind zu einem veränderlichen Spannungsteiler (Widerstand mit Mittelabgriff durch Schleifkontakt) zusammengefasst. Wird dieser als linearer Drehwiderstand ("Potentiometer" ausgelegt, so gilt $R_1 = f(S)$, wenn S den Skalenwert des Abgriffs darstellt. Es gilt für $R_x = R_3 [(S_{maz}/S) - 1]$. Damit wird die R_x -Skala nicht linear. Die Messfehler für diese Schaltung werden diskutiert.

(2) Nur R_2 wird als veränderlicher Widerstand ausgebildet. Mit $R_1 + R_2 = R_0$ und $R_2 = f(S)$ folgt $R_x = [(R_3R_0)/(R_1S_{maz})]S$.

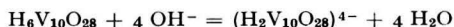
Hier ist R_x linear von S abhängig. Auch für diese Schaltung werden die Messfehler diskutiert.

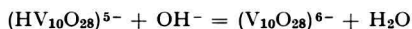
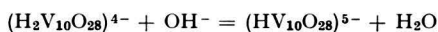
Anschließend erfolgt eine kurze Diskussion der Abgleichsbedingungen für komplexe Widerstände, eine Betrachtung von Erdungsfragen, die speziell bei elektrochemischen Arbeiten von Bedeutung ist, und vom Aufbau des Anzeigeverstärkers.

An Hand einer neu entwickelten Präzisionsmessbrücke für Elektrolytwiderstände werden diese Fragen im Detail diskutiert. [Fr.Oe.]

981 – Conductometric titrations of sodium metavanadate and of free decavanadic acid solutions respectively with mineral acids and sodium hydroxide or ammonia (in German). K. F. Jahr, L. Schoepp and J. Fuchs (Institute of Inorg. Chemistry, The Free University, Berlin, Germany). *Z. Naturforsch.*, 14b (1959) 469.

Decavanadic acid, yellow coloured, is obtained by acidifying sodium metavanadate solution. The relative conductometric titration curve is plotted as a function of the acid base $\text{Na}_2\text{O} : \text{V}_2\text{O}_5$ ratio and consists of four straight lines which cross each other at three points. The free decavanadic acid is obtained by dissolving vanadium oxide in H_2O_2 solution; by titrating this acid with sodium hydroxide or ammonia, the conductometric curve may be plotted. In this case also, the curve consists of four straight lines. The free acid titration occurs according to:



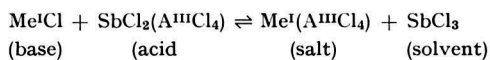


The results are discussed.

[Di.Ciò.]

982 – Molten antimony(III) chloride as an ionizing “water-like” solvent. I (in German). G. Jander and K. H. Swart (Institute of Inorg. Chemistry, Technical University, Charlottenburg-Berlin, Germany). *Z. anorg. u. allgem. Chem.*, 301 (1959) 54.

Reactions, analogous to neutralization, in molten antimony(III) chloride have been studied by conductometric and potentiometric titrations as well as by preparative methods. In these neutralization reactions, only a few SbCl_2^+ and Cl^- ions are formed from dissociated solvent molecules of SbCl_3 , according to:



A deficit of pure acid-type compounds is found in the solution medium, SbCl_3 ; the relative strength of these compounds is either weak or medium. Moreover, pure strong basic-type compounds may be found. In addition to real or potential acids and bases the behavior of some amphoteric chlorides has also been investigated.

[Di.Ciò.]

983 – Molten antimony(III) chloride as an ionizing “water-like” solvent. II (in German). G. Jander and K. H. Swart (Institute of Inorg. Chemistry, Technical University, Charlottenburg-Berlin, Germany). *Z. anorg. u. allgem. Chem.*, 301 (1959) 80.

Solvolytic reactions which appear to be the opposite of neutralization-like reactions have been established for various groups of salts in the solvent SbCl_3 .

SbBr_3 and SbI_3 do not show conductivity in fused SbCl_3 . KBr and KI are soluble in the solvent: the sulphates, like most of the metal sulphides, are insoluble.

Sb_2S_3 is soluble and undergoes partial solvolysis according to: $\text{Sb}_2\text{S}_3 + \text{SbCl}_3 \rightarrow 3 \text{SbSCL}$.

Most of the oxides are insoluble and for the soluble oxides may be written: $3 \text{Me}^{\text{II}}\text{O} + 2 \text{SbCl}_3 \rightarrow 3 \text{Me}^{\text{II}}\text{Cl}_2 + \text{Sb}_2\text{O}_3$.

The solvolysis of carbonates and acetates occurs as follows: $3 \text{Me}^i\text{CO}_3 + 2 \text{SbCl}_3 \rightarrow 6 \text{Me}^i\text{Cl} + \text{Sb}_2(\text{CO}_3)_3$; $\text{Sb}_2(\text{CO}_3)_3 + \text{SbCl}_3 \rightarrow \text{SbOCl} + 3 \text{CO}_2$; $3 \text{Me}^i(\text{CH}_3\text{COO}) + \text{SbCl}_3 \rightarrow 3 \text{Me}^i\text{Cl} + \text{Sb}(\text{CH}_3\text{COO})_3$.

[Di.Ciò.]

984 – Researches on the hydrolysis of the alkali aurates solutions (in English). G. Jander and G. Krien (Institute of Inorg. Chemistry, Technical University, Charlottenburg-Berlin, Germany). *Z. anorg. u. allgem. Chem.*, 304 (1960) 154.

Conductometric titrations, light absorption measurements, ultra-filtration experiments, determinations of ionic weights by means of free diffusion and salt cryoscopy, as well as analytical investigations, show that the hydrolysis of alkali aurates containing the monoaurate ion, $[\text{Au}(\text{OH})_4]^-$, yields gel-like, quickly-aging auric acid. In particular, the conductometric titrations of alkali aurates solutions with HClO_4 show that the aurates are salts of monobasic auric acid. Colloidal aggregates of auric acid of diameters from 100 to 200 μ but no detectable polyaurate ions occur as intermediate products.

[Di.Ciò.]

985 – Some transport properties of aqueous pentaerythritol solutions at 25°. F. J. Kelly, Reginald Mills and Jean M. Stokes (School of Physical Sciences, Australian National University, Canberra and Physical Chemistry Dept., University of New England, Armidale, N.S.W., Australia). *J. Phys. Chem.*, 64 (1960) 1448.

The following properties of aqueous pentaerythritol solutions are measured and discussed: viscosity and density, diffusion coefficient and self-diffusion coefficient, and limiting conductance of sodium and potassium chlorides in the solution.

[D.S.Ru.]

986 – Solutions of metals in molten salts. Cerium in cerium oxide. H. R. Bronstein, A. S. Dworkin and M. A. Bredig (Chemistry Div., Oak Ridge National Laboratory, Oak Ridge, Tenn., U.S.A.). *J. Phys. Chem.*, 64 (1960) 1344.

Investigation of the possible existence of Ce^+ ion in a molten solution of Ce in CeCl_3 has yielded strange electrical conductance values. It was found, however, that a reaction was taking place with the crucible to form CeOCl .

[D.S.Ru.]

987 – Conductances of aqueous solutions of sodium hexanoate (sodium caproate) and the limiting conductances of the hexanoate ion, at 25° and 35°. A. N. Campbell and J. I. Friesen (Chemistry Dept., University of Manitoba, Winnipeg, Manitoba, Canada). *Can. J. Chem.*, 38 (1960) 1939. The equivalent conductances, densities and viscosities of aqueous solutions of sodium hexanoate were determined at 25° and 35° from 0.0003 *M* to saturation. The limiting equivalent conductance of the hexanoate ion was determined as 27.37 ± 0.04 Mhos at 25° (and 34.69 ± 0.05 Mhos at 35°). The Robinson–Stokes equation reproduces the data satisfactorily in dilute solutions, where $a^\circ = 13 \text{ \AA}^\circ$ at 25 and 10 \AA° at 35°. The Falkenhagen–Leist equation reproduces the data similarly when $a^\circ = 5.5 \text{ \AA}^\circ$ at 25° and 4.0 \AA° at 35°. Data indicated that the hexanoate ion does not form ionic micelles. [D.S.Ru.]

988 – Die hochfrequenztitrimetrische Bestimmung von Schwefelwasserstoff und Mercaptanen in technischen Gasen nach Absorption mit Natronlauge. F. Oehme (Inst. Entw. chem.-phys. Analysenmethoden, Weilheim/Obb., Deutschland). *Erdöl u. Kohle*, 13 (1960) 394. Schwefelwasserstoff und Mercaptane werden aus technischen, chemisch neutralen Gasen häufig durch Absorption mit Lauge gebunden. Die hohe Grundleitfähigkeit der Absorptionsflüssigkeit und ihr Basencharakter verbietet eine direkte Titration der genannten Schwefelverbindungen. Bei Passage über die H-Form eines Kationen-Austauschers wird die Lauge jedoch neutralisiert. Zugleich entsteht freier Schwefelwasserstoff und freies Mercaptan, die beide als Summe durch eine Hochfrequenz-Titration mit Bleiacetat erfasst werden. Als Gerät eignet sich das Hochfrequenz-Titrimeter HFT 30 C (WTW) unter Verwendung der Ausschlagsmethode. Der ausfallende Niederschlag von Bleisulfid und Bleimercaptid wird abzentrifugiert und mit Collidin extrahiert. Durch Photometrie der gelben Lösung ergibt sich der Mercaptangehalt. [Fr.Oe.]

989 – Konduktometrische Titraktionen. F. Oehme (Inst. Entw. chem.-phys. Analysenmethoden, Weilheim/Obb., Deutschland). *Mitt. Inst. Entw. chem.-phys. Analysenmeth.* 3 (1960) 60. Für die Durchführung konduktometrischer Titraktionen gibt es eine Reihe von Richtlinien, welche die Brauchbarkeit dieser Analysenmethode begrenzen. Es handelt sich dabei um die Ansprechempfindlichkeit des Leitfähigkeitsmessgerätes und die Grundleitfähigkeit der Probe. Diese kann durch Überführung der zu bestimmenden Komponente in eine organische Phase häufig klein gehalten werden. Auch die Anwendung von Ionenaustauschern kann zum Ziel führen. Beispiele für derartige Anwendungen werden gegeben und mit einer kurzen Besprechung neuer Anwendungen konduktometrischer Titraktionen abgeschlossen. Apparative Angaben über die Wahl geeigneter Titrationszellen, über eine neue Kolbenbürette und verschiedene Rührertypen ergänzen die Ausführungen. [Fr.Oe.]

990 – Appareil enregistreur pour traces d'oxygène. J. Pierrain (Département Contrôle et Recherches de la Société Finalens). *Chim. anal.*, 42 (1960) 78. L'auteur propose un appareil enregistreur basé sur des méthodes colorimétriques d'analyse. Il rappelle les méthodes par conductibilité (R. Egalon, *Chimie & industrie*, suppl. *Génie Chim.*, 81 (1959) 140) et la méthode à l'électrode polarisée. [Bad.Lam.]

991 – Remarks on high-frequency electroconductivity. Solution composition curves (in Russian). V. I. Ermakov. *Zhur. Fiz. Khim.*, 34 (1960) 2258. It has been demonstrated that curves showing the decrease of the oscillographic wave in relation to the composition of the electrolytic solutions, determined with the aid of inductive type cells are free of any significant distortion that might be caused by the method of measurement. The curves should be interpreted on the basis of the high-frequency electroconductivity of the solutions and of the mechanism of their interaction with the electromagnetic field of the cell. [Ot.So.]

See also abstracts nos. 806, 809, 811–813, 817, 839, 841, 847, 852, 853, 855, 858, 895, 1056, 1057

6. Electrolysis

992 – Comparison of two methods of measuring the isotopic effect in the electrolysis of molten nitrates (in German). A. Lundén (Physical Institute, Chalmers Technical University, Göteborg,

nitrate (in German). A. Lundén (Physical Institute, Chalmers Technical College, Göteborg, Germany). *Z. Naturforsch.*, 14a (1959) 801.

The isotopic effect in the electrolysis of molten nitrates has been measured by means of a separator tube, or by asbestos paper electrophoresis when the connection between the cation and anion mobilities is known. In this work the author attempts to give the anionic mobilities for the two methods. The resulting differences between the isotopic effect measured with the two methods are discussed. [Di.Ciò.]

993 – Dosage de gaz et de la vapeur d'eau par micropiles galvaniques. A. Berton. *Bull. soc. chim. France*, (1959) 1453.

L'auteur décrit les améliorations qu'il a apportées à la micropile déjà décrite (pli cacheté no. 1299). Les substances acides ou alcalines peuvent être dosées entre deux électrodes de cuivre oxydé et de plomb entre lesquelles passe un courant d'eau distillée. De même avec des électrodes d'or et de plomb l'électrolyte étant de l'anhydride phosphorique déliquescent, on détecte l'humidité. Des électrodes de plomb/plomb oxydé plongeant dans l'acide sulfurique permettent l'étude de liquides non ionisés (nitrobenzène, pyridine, hydrocarbures). Ces piles peuvent enfin être employées comme récepteurs photosensibles. [J.Des.]

994 – Controlled potential electrolytic determination of copper in lead- and tin-base alloys. B. Alfonsi (Research and Control Laboratory, Auto-Avio, Fiat, Turin, Italy). *Anal. Chim. Acta*, 22 (1960) 431.

The two methods described here allow the determination of copper directly from the acid-dissolved alloy by controlled tension electrolysis; this advantageous analytical technique is excellently described by Lingane (*Electroanalytical Chemistry*, Interscience Publishers, New York, 1953), who also gives a complete bibliography. In lead-base alloys with a high percentage of antimony, double electrolysis may be necessary. In tin-base alloys also, the lead may be determined along with the copper; for these alloys, the method is similar to another described previously which was derived from Lingane's method. Here it is extended to a 5 g sample in order to determine the lead up to a percentage of 0.2%. For lead-base alloys the analysis is also carried out on a 5 g sample because the percentage of copper is generally low. [P.Me.]

995 – Electrolytic determination of microgram quantities of water in paper. R. G. Armstrong, K. W. Gardiner and F. W. Adams (Central Research and Eng. Div., Continental Can Co. Inc., Chicago 20, Ill., U.S.A.). *Anal. Chem.*, 32 (1960) 752.

A procedure has been developed for the determination of water in paper in the 11–200 gamma range. The apparatus consists of a tank of dry nitrogen, a magnesium perchlorate drying tube, a brass micro-oven, a moisture monitor, a flow meter and a recorder in connection with an integrator. The water in the sample is vaporized in the oven by a controlled heating program. The water released is carried by the nitrogen stream into the electrolysis cell and absorbed by a thin continuous film of anhydrous phosphoric acid located between two platinum electrodes. The water is electrolyzed by applying a potential to the electrodes. [Kl.Gr.]

996 – Anodic dissolution of alloys of lead with Sb, Bi and Ag in molten alkalis (in Russian). J. K. Delimarskii and A. A. Kolotii (Institute of General and Inorganic Chemistry, Academy of Sciences, U.S.S.R.). *Ukrain. Khim. Zhur.*, 26 (1960) 16.

The authors have tried to find conditions which would make it possible to separate the components of the remainder left after the electrolytic separation of lead from the eutectic $PbCl_2$ – KCl – $NaCl$. Sb, Bi and Ag are present in this remainder. The method used was electrolysis in molten sodium hydroxide at a temperature of about 500°. It was found that Sb dissolves first and can be separated at all current densities. Pb and Bi dissolve simultaneously at high current densities (1 A/cm²) only and Ag is left in the anodic remainder. Sb is not precipitated at the cathode and Bi and Pb only at high current densities. [Ot.So.]

997 – Electrolytic separation of antimony from molten sulfide (in Russian). J. K. Delimarskii and A. A. Velikanov (State University, Kiev, U.S.S.R.). *Ukrain. Khim. Zhur.*, 26 (1960) 168.

The authors have determined the dissociation voltage of Sb_2S_3 and of the alloy 15% Na_2S –85% Sb_2S_3 using the method of ampere–volt curves. The results are collected in a table which shows the temperature dependence over the range 658 to 860°. A dependence of the current yield on temperature has been found. Maximum current yield is reached at temperatures of 800–860°. Optimum conditions have been determined for electrolysis with graphite electrodes in a nitrogen atmosphere: temperature 800–860°, current density 0.5–2.0 A/cm². [Ot.So.]

See also abstract no. 923.

7. Coulometry

998 – Coulometric determination of CO₂ in gas mixtures. J. Prosz and I. Hegedüs (Inst. of Inorganic Chemistry, Technical University, Budapest, Hungary). *Periodica Polytech.*, 4 (1960) 1.

Verfasser berichten über ein neues Verfahren zur Bestimmung geringer CO₂ Mengen in Gasen. Das Prinzip der Methode ist, dass das CO₂ enthaltende Gasgemisch in einer einfachen Vorrichtung immer auf die gleiche Menge Bariumhydroxyds einwirkt, das in Gegenwart von Phenolphthalein auf elektrolytischem Wege auf weissem Papier hergestellt wird, wobei die Zeitdauer der Neutralisationsreaktion durch Messung der Entfärbungszeit eines scharf umgrenzten roten Ringes bestimmt wird. Die Entfärbungszeit als Funktion der CO₂-Konzentration wird auf einer für die jeweilige Vorrichtung gültigen Kalibrationskurve festgehalten. Durch Vergleich der ermittelten Entfärbungszeiten mit den Werten der Kurve kann die gesuchte CO₂-Konzentration unmittelbar abgelesen werden. Die Methode eignet sich zur Bestimmung von CO₂-Konzentrationen zwischen 0.04 und 1%, und ist hauptsächlich für serienmässig durchzuführende Analysen in der Industrie geeignet.

[E. Juh.]

999 – Current and titration efficiencies of electrically generated manganic ion. A. J. Fenton, Jr. and N. H. Furman (Analytical Methods Research, The Procter & Gamble Co., Cincinnati 17, Ohio, U.S.A.). *Anal. Chem.*, 32 (1960) 748.

The ferric-manganous sulfate dual intermediate system is investigated. The conditions for the anodic generation of tripositive manganese at platinum or gold anodes are studied as a function of acidity, current density and concentration of manganese. The optimal conditions are obtained in sulfuric acid- and phosphoric acid-containing media at a platinum electrode with 0.3–0.4 M manganous sulfate. The ferric-manganous intermediate system gives titration efficiencies of about 99.6–99.9% regardless of whether ferrous or manganic ion is generated first. Current-voltage curves under various conditions are shown.

[Kl.Gr.]

1000 – Coulometric determination of minute quantities of iodide by internal electrolysis (in German). J. Kis and Chr. Schejtanow (Inst. of Inorganic Chemistry, Technical University, Budapest, Hungary). *Periodica Polytech.*, 4 (1960) 163.

Verfasser arbeiteten eine auf dem Prinzip der inneren Elektrolyse beruhende coulometrische Methode zur Bestimmung geringer Jodidmengen aus. Die Bestimmung wurde in der Liptschinskij-Jordanowschen Elektrolysezelle durchgeführt. Die zur Oxydation des Jodids zu Jod erforderliche Strommenge wurde mit Hilfe des durch Prosz und Poós entwickelten Mikroculometers gemessen. Mit der Methode können 30–100 γ Jodidmengen innerhalb einer Zeit von ca. 30 Min mit einem relativen Fehler von weniger als 3% bestimmt werden.

[E. Juh.]

1001 – Coulometric permanganate determination of ferrocyanide and iodide ions (in German). Panta S. Tutundzic, Natalia M. Paunovic and Milan M. Paunovic (Phys. Chem. and Electrochem. Institute, Technical Faculty, and Chem. Institute, Medical Faculty, University of Belgrade, Yugoslavia). *Anal. Chim. Acta*, 22 (1960) 345.

The method previously developed for the coulometric permanganometric micro-determination of hydrogen peroxide (*Anal. Chim. Acta*, 22 (1960) 291, see preceding abstract) has been extended to the quantitative determination of ferrocyanide and iodide ions. The only modifications are the use of a constant current source and potentiometric determination of the end-point. The accuracy is better than 1% in both determinations.

[P.Me.]

1002 – Coulometric permanganate determination of hydrogen peroxide (in German). Panta S. Tutundzic and Milan M. Paunovic (Phys. Chem. and Electrochem. Inst., Technical Faculty, and Dept. of Inorg. Chem., Faculty of Agriculture, University of Belgrade, Yugoslavia). *Anal. Chim. Acta*, 22 (1960) 291.

A method has been developed for the quantitative coulometric permanganometric micro-determination of hydrogen peroxide. It is based on the anodic oxidation of manganous ions into permanganate ions by electrolysis at a tension of 1.40–1.70 V. The permanganate ions react directly with hydrogen peroxide, the end-point being ascertained by the colour changes of the indicators ferroin and nitro-ferroin respectively. For hydrogen peroxide quantities of the order of 1 mg, the accuracy is better than 1%.

[P.Me.]

1003 – Controlled potential coulometric determination of tin. Allen J. Bard (Dept. of Chemistry, Harvard University, Cambridge, Mass., U.S.A.). *Anal. Chim. Acta*, 22 (1960) 577.

Since stannic tin is reduced to the stannous state at tensions of –0.3 to –0.4 V vs. S.C.E., it will interfere during the controlled-tension determination of copper and antimony unless it is

complexed. The reduction of tin(II) at tensions of -0.50 to -0.70 V *vs.* S.C.E. proceeds with 100% current efficiency at a mercury cathode, and may be determined coulometrically in the absence of metals not reduced at these tensions. Pre-reduction at -0.40 V will avoid interference by copper, antimony and bismuth in this determination. Lead, which is reduced at about -0.50 V, will interfere. Finally, by electrolysis at -0.60 to -0.70 V *vs.* S.C.E., tin may be removed prior to the determination of such metals as nickel and zinc. [P.Me.]

1004 – The determination of plutonium in irradiated uranium fuel solutions by controlled-potential coulometry. F. A. Scott and R. M. Peekema (General Electric Co., Richland, Washington, U.S.A.). *Talanta*, 6 (1960) 196. (Only summary. Full report is available as document number HW-58491.) Controlled-tension coulometry has been applied to the determination of plutonium in solutions within the range 0.05–50 g/l. The titrations are performed by direct electrode reactions at the controlled-tension electrode. The electronic equipment and special cells necessary are described. When an ion with a standard redox tension near that of the plutonium couple is known to be present the titration can usually be carried out by the selection of a complexing medium which increases the difference between the electrode tension of the interfering substance and that of plutonium. [Ja.Inc.]

1005 – Titrages coulométriques de mélanges d'acide perchlorique et d'acide acétique en milieu eau-acétone. R. Rosset et B. Tremillon (Laboratoire de Chimie Analytique, Ecole Supérieure de de Physique et Chimie, 10, rue Vauquelin, Paris, France). *Bull. soc. chim. France*, (1959) 139. En milieu eau-acétone (85% d'acétone) l'acide perchlorique peut encore être considéré comme fort alors que l'acide acétique devient beaucoup plus faible que dans l'eau. On peut, en conséquence, neutraliser successivement ces deux acides: les auteurs ont titré ainsi des mélanges acide perchlorique-acide acétique (0.001 M) avec une précision voisine de 1%. La faible solubilité de la soude dans l'acétone, provoquant un phénomène de démixion a conduit les auteurs à préparer les ions HO^- par réduction de l'eau $2 \text{H}_2\text{O} + 2 \text{e} \rightarrow \text{H}_2 + 2 \text{HO}^-$ à une électrode de platine (coulométrie à intensité constante). Les points équivalents correspondant à la neutralisation des deux acides ont été mis en évidence par ampérométrie à tension constante et potentiométrie à intensité constante avec deux électrodes indicatrices de platine platiné. [Bad.Lam.]

1006 – Determination of the valence state of neptunium ions in solution by controlled potential coulometry. R. W. Stromatt (Hanford Lab. Op., General Electric Co., Richland, Wash., U.S.A.). *Anal. Chem.*, 32 (1960) 134. A controlled-tension coulometer connected to a three compartment cell with a platinum gauze working electrode, a saturated calomel comparison electrode, and a platinum wire electrode is used for the coulometric determination of the valence states of neptunium ions. The analysis depends on the fact that Np(IV) is not oxidized at the platinum electrode. 1 M sulfuric acid serves as the electrolyte solution. First Np(VI) is reduced to the (V) valence state and after completion of the reduction Np(V) is oxidized to Np(VI). Then Ce(IV) is added to oxidize Np(IV) to Np(VI) and the excess of Ce(IV) and Np(VI) is reduced electrolytically. All the Np(IV) is then oxidized to Np(VI). The amount of Np present in the valence states IV, V and VI can be calculated from the coulometer readings. [Kl.Gr.]

See also abstract nos. 832, 838, 841, 857.

8. Electrophoresis

1007 – Separation of fast-moving γ -globulins by starch-gel electrophoresis. M. D. Poulik, W. W. Zuelzer and R. Meyer (The Child Research Center of Michigan, The Children's Hospital of Michigan, and the Dept. of Pediatrics, Wayne State University, College of Medicine, Detroit, Mich., U.S.A.). *Nature*, 184 (1959) 1800.

It was found possible to determine portions of fast-moving γ -globulins by filter paper electrophoresis. In this respect, solutions of antigen and normal human serum were subjected to starch gel immuno-electrophoresis in borate buffer and in a discontinuous system of buffers. In the discontinuous system of buffers, two-dimensional zone electrophoresis, conducted on normal human

sera, revealed two distinct protein zones in the region where the β -1-globulin (transferrin) and β -lipoproteins are usually found. [M.K.Hus.]

1008 – Electrophoresis of human gastric juice. R. Gullberg and B. Olhagen (Konung Gustaf V:s Forsknings Institut, Stockholm 60, Sweden). *Nature*, 184 (1959) 1848.

Analysis of the macromolecular components of gastric juice was made by paper electrophoresis. The gastric juice was collected as a fasting secretion or after insulin stimulation. A suction device prevented the admixture of saliva. Samples contaminated with blood or bile were discarded. The juice collected was cooled immediately on ice and treated continuously in the cold. Electrophoresis was substantiated in borate buffer at a pH of 9.0.

It was found that the most rapidly anodically migrating component, which could be stained with amido black, has the same mobility as crystalline pepsin. This component has earlier been shown to be a carrier of peptic activity. [M.K.Hus.]

1009 – Rapid estimations of zone content in paper chromatographs. VI. R.Lf. method. G. G. Blake (Dept. of Chemistry, Sydney University, Australia). *Anal. Chim. Acta*, 22 (1960) 546.

The employment of Blake's "Rectified Low-frequency" circuit for plotting graphs for rapid determinations of the content of chromatographic zones is described. Comparison is made between this and his "Electrostatic Discharge" method. It is seen from graphs that either method may be used over the range required. The R. Lf. circuit presents several advantages for this work in general, but when the solute content is less than one part in 10,000 as is the case when samples of distilled water are to be compared the static discharge method is by far the better. [P.Me.]

1010 – Continuous zone electrophoresis of pituitary extracts. A. L. Wallace and K. A. Ferguson (Div. of Animal Physiol., C.S.I.R.O. Sheep Biol. Lab., Prospect, N.S.W., Australia). *J. Chromatog.*, 4 (1960) 233.

It is suggested that the observed lack of resolution in the separation is due to the formation of protein complexes. Preliminary evidence is given for the distribution of hormone activity. [L.Gi.]

1011 – The electrophoretic mobility and viscosity of poly(acrylic acid) and poly(methacrylic acid). A. R. Matheson and J. V. McLaren (The University, Nottingham, Great Britain). *J. Chem. Soc.*, (1960) 3581.

The electrophoretic mobility of poly(acrylic acid) of molecular weight $2.5 \cdot 10^6$ has been measured as a function of the following factors: concentration; ionic strength; pH. The concentration exerts only a minor influence, the mobility being maximum at ionic strength ≈ 0.075 . The influence of pH has been found to be dependent on the ionic strength: at 0.11 and 0.20 ionic strengths, the mobility increases with increasing pH to a limiting value (corresponding to complete ionisation); on the other hand, at lower ionic strengths, the mobility has a maximum value around pH 7. The maximum molecular extension is about 3-fold on the basis of the Flory-Fox theory. As shown by potentiometric measurements, Katchalsky's theory is substantially verified, but the dissociation constants decrease slightly with increased ionic strength. The behaviour of poly(methacrylic acid) of M.W. $2.71 \cdot 10^6$ is somewhat different: its mobility decreases with increasing concentration, increasing ionic strength, and decreasing pH. [L.Gi.]

1012 – Séparation par migration ionique et électrophorèse (en anglais). H. Martin. *Chimia*, 14 (1960) 202.

Les différentes méthodes de séparation de mélanges par la migration de particules chargées dans un champ électrique — électrophorèse de zone et migration ionique en contre-courant — sont résumées à la base de leur comportement théorique commun. L'application de la méthode par contre-courant, expérimentalement encore peu développée, est expliquée plus en détail par quelques expériences typiques (enrichissement d'isotopes et de terres rares). [De.Mo.]

1013 – Sur la séparation d'isotopes ioniques par électrophorèse dans des gels ayant des pores du même ordre de grandeur que les ions hydratés. C. J. Van Oss, N. R. Beyrard, S. de Mende et M. Bonnemay. *Compt. rend.*, 248 (1959) 223.

Une hydratation différente des ions Li^+ relatifs aux deux isotopes 6 et 7 du lithium doit leur conférer une mobilité électrophorétique différente. Les auteurs ont vérifié cette hypothèse en effectuant le transport par électrophorèse des sels de lithium dans des gels à porosité variable. Dans la fraction de queue on observe un appauvrissement en ^6Li . Les résultats numériques indiqués par les auteurs sont les vitesses de migration du Li^+ à 23° (cm/V/cm/s 10^{-8}) 5.0, 4.0 et 3.3 auxquelles correspondent

respectivement les rapports suivants $^7\text{Li}/^6\text{Li}$ dans la fraction de queue, 11.95, 12.85 et 13.15 (rapport normal $^7\text{Li}/^6\text{Li} = 11.70$). [Bad.Lam.]

1014 – Paper electrophoresis of inorganic anions in sodium carbonate solution. G. B. Belling and R. E. Underdown (S.A. School of Mines and Industries, North Terrace, Adelaide, South Australia). *Anal. Chim. Acta*, 22 (1960) 203.

The electromigration of inorganic anions has been studied in only a few electrolytes. This paper shows that sodium carbonate can be a suitable electrolyte since it is fairly alkaline, has a suitable electrolytic strength and is not volatile. Although this latter feature would preclude the use of indicators to detect the spots it would allow the electrophoresis apparatus to be operated at a higher voltage, thus enhancing the possibility of achieving satisfactory separations. From the results obtained with the 15 anions examined, it would appear that similar separations to those obtained with ammonium carbonate may be achieved using sodium carbonate. Reproducibility is good, being well within 5% in all cases. [P.Me.]

1015 – Une méthode de détermination électrophorétique de la mobilité des anticorps (en anglais). L. A. Hanson, V. Raunio et C. Wadsworth (Département de bactériologie, Université de Gothenburg, Suède, et Département de microbiologie, Université de Turku, Finlande). *Experientia*, 16 (1960) 327.

Les auteurs présentent une méthode simple qui permet de localiser l'activité des anticorps ou des antigènes après électrophorèse. Cette méthode a été appliquée aux hémagglutinines du sérum et du lait, aux antitoxines et hémolysines. [De.Mo.]

1016 – Papier pour l'électrophorèse des protéines solubles des mitochondres du foie de rat (en anglais). G. Ugazio (Institut de pathologie générale, Université de Cagliari, Italie). *Experientia*, 16 (1960) 349.

Par électrophorèse, l'auteur décèle la présence d'au moins 5 constituants protéiques dans l'hydrolysats des mitochondres du foie de rat. Les colorations spécifiques démontrent la présence de 3 fractions lipoprotéiques et autant de fractions glycoprotéiques. Les hydrolysats des mitochondres ont été obtenus par traitement au trilon X-100. [De.Mo.]

1017 – Analyse immunoélectrophorétique de la gonadotropine chorale humaine. R. Got, G. Lévy et R. Bourrillon (Laboratoire de Chimie biologique, Faculté de Médecine, Paris, France). *Experientia*, 15 (1959) 480.

La pureté de la gonadotropine chorale humaine, présentant une activité de 12,000 mg est confirmée par l'analyse immunoélectrophorétique. Les propriétés caractéristiques antigènes de cette hormone sont révélées par cette méthode. [De.Mo.]

1018 – Séparation par électrophorèse sur papier des protéines solubles de sarcosomes du muscle de rat (en anglais). M. A. Dianzani Mor (Institut de pathologie générale de l'Université de Gènes, Italie). *Experientia*, 15 (1959) 461.

Après l'extraction des protéines solubles des sarcosomes du muscle de rat, on a pu séparer 4 fractions protéiques par électrophorèse sur papier (110 V; tampon de diéthylbarbiturate de sodium, pH 8.6; force ionique 0.1; pendant 12 h). Les 4 fractions sont présentes dans le mélange de respectivement: 26.1, 18.4, 33.2 et 22.3% de protéines totales. [De.Mo.]

1019 – Analyse électrophorétique de lait bovin et de fractions protéiques purifiées du lait bovin du point de vue immunologique (en anglais). L. A. Hanson et B. Johansson (Départ. de bactériologie et de biochimie médicale, Université de Gothenburg, Suède). *Experientia*, 15 (1959) 377.

Au moyen de l'électrophorèse, on a pu mettre en évidence à partir du lait de vache, à l'aide de quelques sérums de lapin anti-lait, au moins 12 immuno-précipités. Six d'entre ces précipités étaient sérologiquement apparentés à des protéines du sang (entre autres: albumine et γ -globuline). Des préparations de α -caséine, β -lactoglobuline et α -lactalbumine ont aussi été analysées. [De.Mo.]

1020 – Etude d'une méthode possible de séparation de la γ -caséine par centrifugation à grande vitesse et son identification au moyen de l'électrophorèse sur agar (en anglais). A. K. Deb, K. V. Giri et N. C. Datta (Département de biochimie, Institut des Sciences de Bangalore et du Collège médical de Bangalore, Indes). *Experientia*, 15 (1959) 344.

Après dialyse du lait, au moyen de cellophane, une partie aliquote de lait est centrifugée à 10,000 t.p.m. On obtient une couche solide de corps gras et un sérum. Ces phases sont traitées séparément. L'électrophorèse est effectuée à 250 V et le courant est de 8 mA. Un graphique donne la position

de γ - et de la β -caséine pour le sédiment et pour le sérum. Il montre que la position de la γ -caséine sur le papier est distinct et caractéristique. [De.Mo.]

1021 – Identification des protéines du sérum humain liées au fer, au cuivre et aux hormones de la thyroïde, par électrophorèse sur gel (en anglais). A. C. Allison (Institut National de Recherches Médicales, Londres, Grande Bretagne). *Experientia*, 15 (1959) 281.

L'auteur analyse, au moyen d'électrophorèse sur gel d'amidon, les protéines qui, dans le sérum humain, lient le fer, le cuivre et l'hormone thyroïdienne, en utilisant comme témoins des protéines purifiées et la radioactivité. Le fer est lié par la β -globuline qui dans certaines familles paraît se diviser en deux composants. Le cuivre est lié par la séruloplasmine qui émigre dans la position α_2 rapide. La protéine principale liant la thyroxine est la préalbumine. [De.Mo.]

1022 – Electrochromatographie sur papier des acides aminés du sérum sanguin (en allemand). V. Jirgl (Institut de l'hématologie et de transfusion sanguine, Prague, Tchécoslovaquie). *Experientia*, 15 (1959) 235.

Une méthode simple pour l'électrochromatographie des acides aminés libres du sérum du sang est proposée. On effectue une séparation dans une première direction au moyen d'un appareil ordinaire à bas voltage. Les acides aminés sont ainsi séparés en composants acide, neutre et basique. On parfait cette séparation en les orientant dans une seconde direction par la technique de chromatographie descendante. Des graphiques sont donnés qui permettent de connaître la position sur le chromatogramme de chaque acide aminé. [De.Mo.]

1023 – Etude immunoélectrophorétique de l'uromucoïde J. P. Vaerman et J. F. Heremans (Cliniques universitaires St-Pierre, Service de Médecine interne, Louvain, Belgique). *Experientia*, 15 (1959) 228.

Des urines de concentration normale ont été étudiées par la technique immunoélectrophorétique, en utilisant un antisérum de l'uromucoïde. Une ligne unique de précipitation est observée qui présente portant deux maxima distincts dont les auteurs donnent une explication qui paraît satisfaisante. [De.Mo.]

1024 – Analyses immunoélectrophorétiques des fractions protéiques du sérum humain séparées par électrophorèse sur gel d'amidon. J. M. Fine et J. Loeb (Centre National de transfusion sanguine, Paris, France). *Experientia*, 15 (1959) 59.

Les constituants du plasma humain, séparés par électrophorèse sur gel d'amidon sont élués et concentrés par lyophilisation. L'analyse immunoélectrophorétique montre que certaines de ces fractions sont hétérogènes du point de vue immunologique. Elles sont constituées d'un mélange en proportions inégales d'un constituant principal et de constituants qui sont voisins immédiats ayant une mobilité légèrement différente que celle du constituant principal. [De.Mo.]

1025 – Denaturing of serum proteins and lipoproteins. I (in Italian). C. Ambrosino and J. Liberatori (Institute of Phys. Chemistry, University of Turin, Italy). *Ann. chim. (Rome)*, 49 (1959) 996.

Electrophoretic measurements are performed on denatured serum proteins, after heating to 110° in the presence of ethylene-, propylene- or butylene-glycol. Under such conditions, especially when using ethylene- or 1,3-butylene-glycol, no coagulation is observed at all and the formation of the "C" component is shown, the concentration of which increases with increasing temperature; the mobility of this component is half-way between those of α - and β -globulins. [Fr.Pan.]

1026 – Denaturing of serum proteins and lipoproteins. II (in Italian). C. Ambrosino, J. Liberatori, G. Lenti and A. Calciati (Institute of Phys. Chemistry, University of Turin, Italy). *Ann. chim. (Rome)*, 49 (1959) 1011.

Following a previous paper on this subject (see preceding abstract), experiments on immuno-electrophoresis on agar are performed in accordance with the Grabar method. Evidence is given for normal proteins when serum is denatured by heating in the presence of glycols. Conclusions are drawn that, apart from the formation of the "C" component, the electrophoretic and immuno-chemical properties of some proteins do not undergo any change. [Fr.Pan.]

1027 – Electrophoresis of inorganic complexes in solution. IV. Determination of the equivalent weight of complex electrolytes (in Italian). V. Carassiti and M. Claudi (Istituto Chimico "G. Ciamician", University of Bologna, Italy). *Ann. chim. (Rome)*, 49 (1959) 2149.

The moving boundary method is generally used when determinations of transfer numbers have to be carried out with great accuracy. In this paper the reliability of such a method for the determination of equivalent weights in complex electrolytes has been tested. For this purpose the

motions of both the anionic and cationic boundaries are recorded. Optimum experimental conditions are discussed. [Fr.Pan.]

1028 – Starch gel electrophoresis of wheat proteins. G. A. H. Elton and J. A. D. Ewart (British Baking Industries Research Association, Chorleywood, Herts., Great Britain). *Nature*, 187 (1960) 600.

Experiments are carried out to replace the use of the Tiselius apparatus for examining the proteins of the gluten complex of wheat by the electrophoresis method. Wet gluten is prepared from wheat flour and is then dispersed in acetic acid by a high speed stirrer. The liquid is subjected after sometime to starch gel electrophoresis. Runs are normally made for 2–4 h at a potential gradient of 4–6 V/cm. The work shows that starch gel electrophoresis is a valuable method for investigating wheat protein. [M.K.Hus.]

1029 – Two-dimensional high voltage paper electrophoresis of amino and other organic acids. D. Gross (Tate and Lyle Research Lab., Keston, Kent, Great Britain). *Nature*, 184 (1959) 1298. A separation of amino acids can be substantiated by electrophoresis. A higher degree of resolution and a greater certainty of identifying the compounds separated, however, can be attained by the adoption of a two-dimensional technique, that is, subjecting the sample to electrophoresis on the same sheet under two different pH conditions with consequently differing migration patterns. The most suitable procedure is described in detail and the pattern of 27 amino acids and amides separated by this technique is shown. The two-dimensional technique is also successively tried for the resolution of complex mixtures of organic acids by choosing three well-tested buffer or electrolyte solutions of pH 2.0, 4.0 and 8.9 having different rates and sequences of migration. [M.K.Hus.]

1030 – Paper electrophoretic patterns obtained by paraffin oil fixation. H. Waldmann Meyer (Biological Institute of the Carlsberg Foundation, Copenhagen, Denmark). *Nature*, 184 (1959) 1567. It was observed that, during the staining of paper electrophoretic patterns, paraffin oil is strongly adsorbed to heat-denatured proteins and thus gives rise to water repellent protein–dye complexes. This fact permits a method to be devised by means of which the total area occupied by each fraction of a protein mixture can be seen as a sharply delimited zone against a totally white background. The procedure for staining and treatment is given in detail. It was found that by this technique, each serum shows a characteristic pattern. Up to five globulin fractions appear clearly distinguishable. The migration end-points of the individual fractions can be easily determined by visual inspection. On comparing the results obtained with those achieved planimetrically, the biggest difference was found in the albumin γ -globulin ratios due to the adsorption of protein, while close agreement could be noticed in barbital buffer of pH 8.6 where γ -globulin adsorption is considerably reduced. [M.K.Hus.]

1031 – Electrophoretic heterogeneity of trypsin. J. C. Perrone, L. V. Divitger and A. Iachan (National Technological Institute, Rio de Janeiro, Brazil). *Nature*, 184 (1959) 1225.

An investigation regarding the paper electrophoretic behaviour of crystalline trypsin and the trypsin fraction is made. It is shown that the behaviour of crystalline trypsin in free-boundary electrophoresis at pH 2.5 is fundamentally similar to that obtained with paper electrophoresis. The results obtained indicate that trypsin contains at least four distinct electrophoretic fractions, F_1 and F_2 migrating together as the main component during paper electrophoresis at pH 2.6, and which can be separated only in the presence of calcium at pH 5 by free electrophoresis; and fractions F_3 and F_4 which are resolved directly by paper electrophoresis at pH 2.6. An important point is that the fraction obtained by paper electrophoresis at pH 2.6 seems to bear no relation to those given by free electrophoresis at pH 5 in the presence of calcium. No conclusive evidence exists for identifying F_2 obtained by direct electrophoresis of crystalline trypsin, with F_2 resulting from the fractionation of the main component separated by paper electrophoresis, inasmuch as their mobilities are different. At pH 2.5 both trypsin fractions react with calcium ions. [M.K.Hus.]

1032 – Starch–agar gel electrophoresis of tuberculo-proteins from heated culture fibres. T. P. Dekker (Central Veterinary Institute, Rotterdam, The Netherlands). *Nature*, 186 (1960) 392.

A starch gel electrophoresis method for determining the protein composition in a tuberculin purified protein derivative precipitated with trichloroacetic acid from heated culture fibres is given. The agar is weakened in a special buffer solution, made up to pH 7.5, and the agar is then dissolved by boiling. After cooling, starch is added and the solution heated with stirring and boiled for a few seconds. The liquid gel is then poured out into trays which are placed in the electrophoresis apparatus containing platinum electrodes. Using a special arrangement, immediately after adding the protein solution the gels are subjected to electrophoresis at room temperature for 17 h

at 6 V/cm. They are then left to stain with Bayers "Amidoschwarz 10 B" for 15 min, washed with the same solution over a period of 1 h, and then the process is repeated about 5 times with fresh solutions. [M.K.Hus.]

1033 – High voltage paper electrophoresis of aliphatic amines and related compounds. D. Gross (Research Lab., Tate and Lyle Ltd., Keston, Kent, Great Britain). *Nature*, 184 (1959) 1633. Separation of amines by paper electrophoresis at a potential gradient of 10 V/cm and pH 3.8 was carried out successfully. The designing of suitable equipment which allows the simultaneous running of up to 12 samples has facilitated sharp separations of closely neighbouring members of a homologous series and their further identification by means of sufficient reference compounds. The feasibility of separating the members of the mono-alkylammonium series was graphically indicated. However, an actual separation of a mixture of alkylamines of C₁–C₁₀ has never been obtained. The slight retardation in the migration rates of the compounds in the mixture, compared with their individual migration rates is a concentration effect due to heavier loading and mutual ionic interference. [M.K.Hus.]

1034 – Determination of the fibrinogen content of blood plasma by paper electrophoresis. S. M. Shevchenko (I. M. Schenov Medical Inst., Moscow, U.S.S.R.). *Lab. Delo*, 5 (1959) 25. A 0.01 ml serum sample is used, the buffer being at pH 9.3, the applied voltage 210 V for 18 h, and the staining carried out with C.I. acid black 1 (200 mg) in methanol (100 ml) and acetic acid (900 ml) after placing the paper in a desiccator at 105–110°; this is followed by development with phenol (4% in 10% acetic acid). Elution can be done with 0.1 N NaOH, and the result read from a colorimeter provided with an orange filter. [Ca.Cas.]

1035 – Electrophoretic behaviour of serum amylase. Determination of amylase. R. L. McGeachin and J. P. Lewis (Dept. of Biochem., School of Medicine, University of Louisville, Ky., U.S.A.). *J. Biol. Chem.*, 234 (1959) 795. A previous method (Van Loon *et al.*, *Am. J. Clin. Pathol.*, 22 (1959) 1134) is improved by reducing the original sample and reagents to 1/10 and by using barbitone buffer (pH 7.6) instead of a phosphate buffer. The starch–I₂ complex is evaluated spectrophotometrically at 660 m μ . [Ca.Cas.]

1036 – Demonstration of plasma fibrinogen by paper electrophoresis. G. A. Cheyne (Obstet. Med. Research Unit, M.R.C., University of Aberdeen, Scotland). *Lancet*, (1959 I) 763. A good separation of fibrinogen from fibrin can be achieved in the following way: electrophoresis of heparinised plasma is carried out under the usual conditions (8 mA, 24 h) after which the polarity is reversed and electrophoresis is again carried out with increased current (12 mA) for 1.5 h. [Ca.Cas.]

1037 – Ethane-diol and propane-1 : 2-diol in the pre-staining of lipoproteins for electrophoresis. H. J. McDonald and L. P. Ribeiro (Graduate School and Stritch School of Medicine, Loyola University, Chicago, Ill., U.S.A.). *Clin. Chim. Acta*, 4 (1959) 458. To an 0.5 ml sample is added 0.1 ml of a dye solution (prepared by heating ethane-diol or propane-1,2-diol at 100–110°, adding 1% of C.I. solvent black 3, stirring for 5 min, filtering while hot, and when cool adding more dye; after 45 min at room temperature the excess dye is removed by centrifuging); electrophoresis is then carried out on Whatman 3MM paper, using about 0.01 ml of solution per cm of paper. Quantitative results are obtained. [Ca.Cas.]

1038 – Borate buffer in zone electrophoresis. R. Havez and G. Biserte (Laboratory of Chem. Biology, Combined Faculty of Med. and Pharm., Lille, France). *Clin. Chim. Acta*, 4 (1959) 334. Interaction between borate ions and proteins is responsible for the changes observed in the migration rates of proteins when borate buffer is used according to Smithies (*Biochem. J.*, 61 (1955) 629); with immunological methods, prealbumin fractions are detectable. [Ca.Cas.]

1039 – Investigation of the correlation between the results of electrophoresis of serum proteins on paper, on starch gel and by immunoelectrophoresis. J. Moretti, G. Boussier, M. P. Hugon and L. Hartmann (Biochem. Lab., Faculty of Medicine, Paris, France). *Bull. soc. chim. biol.*, 41 (1959) 79. From experiments based on several pathological sera, the following conclusions were obtained: a slightly better resolution, particularly in the case of globulins, can be achieved in immunoelectrophoresis (which gives 19 detectable components, of which 11 have been identified) than in starch gel electrophoresis (18 bands); a correlation between these latter bands and the five bands detectable in paper electrophoresis has been established; lipoproteins are not developed by

C.I. acid black 1 and only faintly by C.I. solvent black 3 in immunoelectrophoresis. It is advisable, in clinical practice, to choose the method on the basis of the data to be established.

[Ca.Cas.]

1040 – The separation of some inorganic ions by high-voltage electromigration in paper. R. A. Bailey and L. Yaffe (Radio Chemistry Laboratory, Dept. of Chemistry, McGill University, Montreal, Canada). *Can. J. Chem.*, 38 (1960) 1871.

A number of inorganic ions have been separated by high-voltage electromigration in paper. The systems considered include some of particular radiochemical interest, such as Sr–Y, Ba–La, Mo–Tc, Pb–Bi–Po, as well as alkali metals, and some elements of the first long period. Background electrolytes were usually solutions of complex-forming organic acids. [D.S.Ru.]

See also abstracts nos. 824, 828–830, 843, 844, 856.

9. Other methods

1041 – Intermolecular effects in solutions of methyl isobutyl ketone in alcohols and fluoroalcohols.

Hartley C. Eckstrom, Jerry E. Berger and Lyle R. Dawson (Dept. of Chemistry, University of Kentucky, Lexington, Ky., U.S.A.). *J. Phys. Chem.*, 64 (1960) 1458.

The dielectric constants and the partial molar volumes were determined for mixtures of methyl isobutyl ketone and each of six alcohols: $\text{CF}_3\cdot\text{CHOH}$, $\text{HCF}_2\cdot\text{CF}_2\cdot\text{CH}_2\text{OH}$, $\text{HCF}_2\cdot(\text{CF}_2)_3\cdot\text{CH}_2\text{OH}$, $\text{C}_2\text{H}_5\text{OH}$, $n\text{-C}_3\text{H}_7\text{OH}$ and $n\text{-C}_5\text{H}_{11}\text{OH}$. Polarizations calculated from the Syrkin equation as a function of the concentration may be interpreted as showing that the ketone molecule has a greater ability to form hydrogen bonds with the polyfluoroalcohol molecules than their corresponding hydrocarbon analogs. [D.S.Ru.]

1042 – Dielektrische Messungen an Kohlenwasserstoffölen. F. Oehme (Inst. Entw. chem.-phys. Analysenmethoden, Weilheim/Obb., Deutschland). *Erdöl u. Kohle*, 13 (1960) 740.

Im Gegensatz zu Isolierölen, welche in ihrer Oxydationsneigung durch eine Messung des dielektrischen Verlustfaktors $\tan \delta$ im Gebiet der niederfrequenten Leitfähigkeitsverluste gekennzeichnet werden können, zeigen Schmieröle im allgemeinen bereits im Frischzustand so hohe Leitfähigkeitsverluste, dass eine oxydative Alterung keinen zusätzlichen Effekt bringt. Er ergab sich jedoch, dass praktisch alle bisher untersuchten Schmieröle im Frequenzgebiet von einigen MHz Debye-Verluste zeigen. Bei der oxydativen Alterung der Öle nimmt das Maximum von $\tan \delta$ in charakteristischer Weise zu. Der Gradient dieser δ -Zunahme kann zur Beurteilung der Oxydationsneigung eines Öles bzw. der Wirksamkeit eines Additives hinsichtlich des Oxydationsschutzes herangezogen werden. Diese Vorstellungen werden theoretisch begründet und mit Diagrammen von Ölalterungen nach dem Indiana- und Baader-Test belegt. Alle Messungen wurden bei 20° mit einem Multi-Dekameter im Frequenzbereich von 100 kHz bis 12 MHz vorgenommen.

[Fr.Oe.]

1043 – Abhängigkeit der Dielektrizitätskonstanten (DK) von der Hydroxylzahl bei Fettalkoholen F. Oehme (Inst. Entw. chem.-phys. Analysenmethoden, Weilheim/Obb., Deutschland). *Fette u. Seifen*, 62 (1960) 910.

Die Dielektrizitätskonstante einwertiger aliphatischer Alkohole hängt in einfacher Weise von der Kohlenstoffzahl ab (R.S. Phadke, *J. Indian Inst. Sci.*, 34 (1952) 293). Daraufhin war zu erwarten, dass ein ähnlicher Zusammenhang zwischen der DK und der Hydroxylzahl besteht. Entsprechende Untersuchungen wurden mit höheren aliphatischen Alkoholen (bis C-20) an Reinsubstanzen und technischen Proben vorgenommen. Die bei 90° mit einem Dekameter DK 03 (WTW) durchgeführten Messungen zeigen, dass die Provenienz der Alkohole eine bestimmende Rolle auf die DK ausübt, was auf einen Gehalt an Isomeren, sowie an Paraffinkohlenwasserstoffen zurückzuführen ist. Die dadurch bedingten Schwankungen sind jedoch nicht so gross, dass nicht trotzdem DK-Messungen in der Betriebskontrolle zur Bestimmung der Hydroxylzahl herangezogen werden könnten. Dagegen zeigt der Temperaturkoeffizient der DK erheblich grössere Streuungen, so dass eine analytische Auswertung nicht in Frage kommt. [Fr.Oe.]

1044 – Impedance of a suspension of spherical particles. A model for the dielectric behavior of cell suspensions and protein solutions (in German). H. Pauly and H. P. Schwan (University of Pennsylvania, Philadelphia, Pa., U.S.A.). *Z. Naturforsch.*, 14b (1959) 125.

The frequency dependence of the dielectric behavior of a suspension of spherical particles has been investigated. The general solutions and the approximation formulae are given. The frequency behavior is exactly fixed by means of two relations of Debye–Typ. These formulae permit the impedance curve analysis of cell suspensions of bacteria, protein solutions, and other suspensions. [Di.Ciò.]

1045 – Die Wasserbestimmung in Pigment-Pasten und Druckfarben nach einer modifizierten Extraktionsmethoden. F. Oehme (Inst. Entw. chem.-phys. Analysemethoden, Weilheim/Obb., Deutschland). *Farbe u. Lack*, 66 (1960) 142.

Die technisch wichtige Wasserbestimmung auf der Grundlage eines Trocknungsverfahrens befriedigt bei Pigmentpasten und Druckfarben nur selten. Abgesehen von relativ langen Trocknungszeiten, besteht immer die Gefahr, dass bei fertigen Pigmentanreibungen sich ausser Wasser noch andere Bestandteile verflüchtigen können. Die naheliegende Anwendung der sogenannten Extraktionsmethode unter Extraktion des Wassers mit Dioxan und dessen quantitativer Bestimmung aus der Erhöhung der Dielektrizitätskonstanten (DK) des Extraktes, liefert ebenfalls nur selten fehlerfreie Resultate, da speziell bei organischen Pigmenten häufig Anteile gelöst werden und die DK des Extraktes zusätzlich beeinflussen. In einer Modifikation dieser Methode unter Trocknung des Extraktes über eine Säule eines geeigneten Molekularsiebes kann jedoch aus der DK-Abnahme bei der Trocknung die Wasserbestimmung mit guter Genauigkeit vorgenommen werden. [Fr.Oe.]

1046 – Determination of active oxygen in metalo-ceramic charged nickel electrodes (in Russian). I. S. Mustafin and N. S. Frumina (State University, Saratov, U.S.S.R.). *Zavodskaya Lab.*, 26 (1960) 410.

The authors have tried to find a reducing agent which would react with higher nickel oxides in alkaline media. Tartaric acid and Cr^{3+} salts have proved suitable. There are no direct methods known for the determination of tartaric acid and therefore the reaction with Cr^{3+} salts has been used. Heating helps the course of the reaction. Cr^{3+} is oxidised to chromate, which is determined after acidification iodometrically or reductometrically using Mohr's salt. [Ot.So.]

1047 – Kinetics of electrode processes on solid electrodes. II. Analysis of oscillograms obtained with a nickel electrode in sulphuric acid solutions during changes in anodic current densities (in Russian). V. I. Kravtsov and Chang-Chih-Bing. *Zhur. Fiz. Khim.*, 34 (1960) 2205.

The anodic oscillograms obtained with a nickel electrode during decrease of the polarisation current density in 1 N and 10 N H_2SO_4 solutions are in satisfactory agreement with equations based on the slow discharge theory. The considerable deviation from analogous oscillograms obtained during increase of the anodic current density has been explained by the depolarizing effect of atomic hydrogen which takes part in the anodic process together with the nickel atoms. A method for calculating the capacity of the electrical double layer has been proposed on the basis of the analysis of the oscillograms obtained during change in polarization current density. It has been shown that when a moving coil oscillograph is used, the proposed method gives more reliable results than that commonly used for determining the capacity of the electrical double layer from the slopes of the initial portions of the curves. [Ot.So.]

See also abstracts nos. 822, 842.

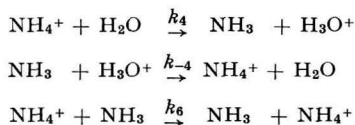
10. Related topics

1048 – The dielectric polarizations and apparent dipole moments of alcohols as solutes. R. J. W. Lefevre and A. J. Williams (University of Sidney, Australia). *J. Chem. Soc.*, (1960) 108.

14 normal alcohols (together with cyclopentyl and cyclohexyl) have been studied in CCl_4 at 25°, and some in benzene. The calculated values of dipole moments are slightly higher than those reported in earlier literature. Some empirical equations are proposed, to deal with the influence of the number of carbon atoms in the alkyl chain. [L.Gi.]

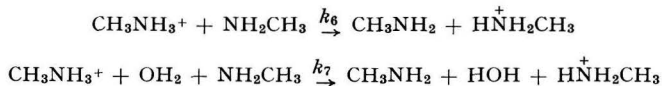
1049 – Dielectric relaxation times for normal alcohols at infinite dilution in CCl₄ and benzene. R. J. W. Lefevre and A. J. Williams (University of Sidney, Australia). *J. Chem. Soc.*, (1960) 1115. The calculated relaxation times of the alcohols under consideration (see preceding abstract) are in substantial agreement with an equation proposed by Chau, Lefèvre and Tardif. Discontinuities observed in the loss tangent *vs.* concentration curves are attributed to the occurrence of association. [L.Gi.]

1050 – Proton-transfer studies by nuclear magnetic resonance. I. Diffusion control in the reaction of ammonium ion in aqueous acid. Merle T. Emerson, Ernest Grunwald and Robert A. Kromhout (Florida State University, Tallahassee, Fla., U.S.A.). *J. Chem. Phys.*, 33 (1960) 547. By precise nuclear magnetic resonance techniques, the rate constants were determined for the reactions:



in aqueous acid at 25°. The results for 0.25–3.00 *M* NH₄Cl are: $k_{-4} = 4.3 \cdot 10^{10} \text{ sec}^{-1} \text{ mole}^{-1}$; $k_6 = 1.17 \cdot 10^9 \text{ sec}^{-1} \text{ mole}^{-1}$; $k_4 = 24.6 \text{ sec}^{-1} \text{ mole}^{-1}$ at zero ionic strength. The order of magnitude of k_{-4} suggests that these reactions are diffusion-controlled. The data in strong acid suggest that rotation of a molecule during an encounter is improbable; during the approach of reactants the unshared electrons of NH₃ face an acidic hydrogen. The value of k_6 suggests a mechanism in which NH₃ and NH₄⁺ become next-nearest neighbors by simple diffusion. The reaction with rate constant k_4 is activation-controlled. [G.Mar.]

1051 – Proton-transfer studies by nuclear magnetic resonance. II. Rate constants and mechanism for the reaction CH₃NH₃⁺ + OH₂ + NH₂CH₃ in aqueous acid. Ernest Gronwald, Photios J. Karabatsos, Robert A. Kromhout and Lee Purlee (Florida State University, Tallahassee, Fla., U.S.A.). *J. Chem. Phys.*, 33 (1960) 556. Rate constants were measured by precise nuclear magnetic resonance techniques for the reactions:



in aqueous acid at 25°. The results are $k_8 = 4.0 \cdot 10^8$ and $k_7 = 5.3 \cdot 10^8 \text{ sec}^{-1} \text{ mole}^{-1}$ for CH₃NH₃⁺ in water at 25° and infinite dilution. For 1.7 to 9.0 *M* solutions of CH₃NH₃Cl in water, acid dissociation constants, densities, viscosities and water activities were also measured. The magnitude of k_7 and the constancy of k_7/k_8 suggest that the most probable rate-determining step for the second reaction is proton transfer from a water molecule to a molecule of CH₃NH₂. [G.Mar.]

1052 – Electrochemical determination of the metals of the vanadium sub-group (in Russian). T. I. Konoutschuk and I. B. Barmashenko (Polytechnical Institute, Kiev, U.S.S.R.). *Ukrain. Khim. Zhur.*, 26 (1960) 25.

The author has studied hydrogen overvoltage on smooth and porous electrodes made from metals of the vanadium sub-group in alkaline and acid media. He found that the dependence of overvoltage on log *i* is linear for smooth and porous Nb and Ta electrodes in acid media and for smooth electrodes in alkaline media. The slope of the curves is 0.12 in acid, and 0.15 to 0.14 in alkaline media. The overvoltage curve for vanadium electrodes has two linear parts with slopes of 0.04 and 0.14. The overvoltage curves for Nb and Ta porous electrodes do not have linear character. [Ot.So.]

1053 – The temperature influence on mercury electric-endosmosis (in German). H. Knof and A. Klemm (Max-Planck Institute for Chemistry, Mainz, Germany). *Naturforsch.*, 14a (1959) 1020. The mercury electrokinetic mobility α is $1.7 \cdot 10^{-3} \text{ cm}^3/\text{V} \cdot \text{sec}$ at –20°; this mobility reaches a maximum ($4.0 \cdot 10^{-3} \text{ cm}^2/\text{V} \cdot \text{sec}$) at 165° and decreases again to $3.0 \cdot 10^{-3} \text{ cm}^2/\text{V} \cdot \text{sec}$ at 278°. This is in accord with the theory that α is essentially proportional to $\lambda_{\infty}^2/\eta_{\infty}$ (λ_{∞} is the mean free-path of the principal electrons; η_{∞} is the viscosity). α depends also on the wall material (glass, iron, platinum, germanium). [Di.Ciò.]

1054 – Anodic reductions. VI. Electrolysis of benzophenone in pyridine solutions between aluminum electrodes. Tsu Tsu Tsai, William E. McEwen and Jacob Kleinberg (Chemical Laboratory, University of Kansas, U.S.A.). *J. Am. Chem. Soc.*, 82 (1960) 3326.

Bei der anodischen Oxydation von Aluminium in Pyridinlösungen von Natriumjodid oder Lithiumchlorid und Anwesenheit von Benzophenon, beobachtet man für die Aluminiumoxydation zu kleine Valenzzahlen. Gleichzeitig konnten aus dem Anodenraum die Reduktionsprodukte des Benzophenons, Benzhydrol und Benzopinakol, isoliert werden. Die isolierbaren Mengen dieser Produkte stehen im Einklang mit der nicht zur Oxydation gebrachten Menge Aluminiums. Ausserdem wurde ein Zusammenhang zwischen reduzierter Menge Benzophenon und Elektrolytkation gefunden. Im Kathodenraum wurden, bei Verwendung von Lithiumchlorid als Elektrolyt, die gleichen Reduktionsprodukte des Benzophenons angetroffen. Es werden verschiedene Reaktionsmechanismen für die Vorgänge im Anoden- und Kathodenraum diskutiert. [Ha.Re.]

1055 – Dependence of the electric conductivity of MgO–Cr₂O₃ mixtures on the conditions of the preceding sintering process (in German). A. Bielansky, J. Dereń and Z. Barutowicz (Institute for Inorg. Chemistry, Academy of Mining and Metallurgy, Krakow, Poland). *Z. anorg. u. allgem. Chem.*, 305 (1960) 169.

The dependence of the electric conductivity of 1:1 MgO–Cr₂O₃ mixtures on the conditions of the preceding sintering process (300–1300°) has been investigated. The results, together with additional chemical, X-ray, microscopic and other investigations, are discussed. [Di.Ciò]

1056 – Electrical conduction in magnesium oxide. Hermann Schmalzried (Max-Planck Institute for Phys. Chemistry, Göttingen, Germany). *J. Chem. Phys.*, 33 (1960) 940.

The tension of the cell: Pt | Fe, FeO | MgO | Ni, NiO | Pt in thoroughly purified nitrogen has been measured. If MgO were an electronic conductor, the tension of this cell would be equal to zero. At 1100°, the tension of the cell was found to be 0.285 ± 0.010 V. It must be concluded, therefore, that MgO is predominantly an ionic conductor at 1100° and the oxygen partial pressure lies between the dissociation pressures of FeO and NiO. No decision is possible as to whether cation or anion conduction in MgO prevails. [G.Mar.]

1057 – Comments on Dr. Schmalzried's letter: Electrical conduction in magnesium oxide. S. P. Mittoff (Metallurgy and Ceramics Research Dept., General Electric Research Laboratory, Schenectady, New York, U.S.A.). *J. Chem. Phys.*, 33 (1960) 941.

The author has duplicated Dr. Schmalzried's experiment (*cf.* preceding abstract) using a Norton crystal of MgO in contact with Fe, FeO and Ni, NiO pellets. He found an equilibrium tension of 0.235 V, whereas he found 0.285 V using ZrO₂ in place of MgO.

In agreement with Dr. Schmalzried, the author concludes that the conduction of MgO is predominantly ionic; however, the lower voltage indicates that about 17% of the current is simultaneously carried by electronic conduction. [G.Mar.]

1058 – Electrochemistry of sulfate-reducing bacteria: cathodic control (in Italian). D. Gherardi, G. Bombara, G. Banfi and V. Cavazzoni (Centre for Microbiology of Fermentation, Milan, Italy). *Ricerca sci.*, 30 (1960) 711.

Following a previous paper on this subject (see abstract No. 232, Vol. 1), steel corrosion in sea water in the presence of sulfate-reducing bacteria is investigated. The addition of nearly 0.75% hydrazine sulfate for deoxygenation appears to reduce the activity of bacteria, as well as pH lower than 6. Cathodic protection can be carried out with a $60 \mu\text{A}/\text{cm}^2$ current and a 200 mV more negative potential. [Fr.Pan.]

1059 – Recherches sur l'obtention, la séparation et la purification du tantalé et du niobium, notamment par voie électrolytique (en français). R. Monnier et P. Grandjean (Laboratoire de chimie et d'électrochimie techniques, Université de Genève, Suisse). *Helv. Chim. Acta*, 43 (1960) 2163.

Une méthode pour la détermination des tensions effectives d'électrolyse utilisant notamment un oscillographe cathodique et un dispositif à transistors pour la coupure du courant et pour la synchronisation des opérations, a été mise au point; elle permet d'établir quasi simultanément les courbes tensions aux bornes resp. tensions effectives courant. Par extrapolation de la partie rectiligne de ces courbes sur l'axe des X (tensions) on obtient des valeurs bien reproductibles des tensions pratiques de décomposition.

Cette méthode a été appliquée avec succès aux solutions cryolithiques de Al₂O₃, Ta₂O₅, Nb₂O₅, et V₂O₅ à 1040°; les valeurs des tensions de décomposition ainsi déterminées sont respectivement de 1.45, 0.91, 0.64 et 0.60 V. [De.Mo.]

1060 – Chromatographie von Polyelektrolyten. VI. Protein-chromatographie auf Ionenaustauscher-Cellulosederivaten. G. Semenza (Physiologisch-Chemisches Institut, Universität Zürich, Helvetia). *Chimia*, 14 (1960) 325.

The various cellulose derivatives that have been suggested for the chromatography of proteins are reported and their different properties discussed. Since artefacts easily arise in ion-exchange chromatography of proteins, suggestions are given and discussed for the correct regeneration of the columns, for the best control of pH and ionic strength during the chromatographic experiments. The elution procedures and schemes are stated and discussed. Finally, several examples of application are quoted. Some 250 literature references are given. [De.Mo.]

1061 – Détermination expérimentale de deux tensions sur des membranes non intra-permutables (en allemand). W. Kuhn, D. H. Walters, H. Majer et H. Eglin (Institut de chimie-physique de l'Université de Bâle, Suisse). *Experientia*, 15 (1959) 275.

Il a été montré expérimentalement que deux différentes tensions apparaissent à travers une membrane "intra-non-permutating" quand deux différentes solutions (par ex.: une solution 0.1 M de NaCl et 0.0001 N KCl et une solution 0.1 N KCl et 0.0001 N NaCl) sont séparées par une telle membrane et quand les pores de cette membrane sont fournis par des ions de l'une ou l'autre des solutions (dans ce cas: essentiellement avec Na⁺ pour la première solution et avec K⁺ la seconde). [De.Mo.]

1062 – Examination of electrode processes occurring during the solution of chromium in sulfuric acid.

L. Kiss (Institute of Physical Chemistry, L. Eötvös University, Budapest, Hungary). *Magyar Kém. Folyóirat*, 65 (1959) 431.

The electrode processes taking place when electrolytic and metallurgical chromium are dissolved in 1.0 N sulfuric acid were investigated with the aid of cathodic and anodic polarization curves. From the experimental results it can be concluded that stresses existing in the crystal lattice increase the overvoltage of the cathodic process (hydrogen evolution) and decrease that of the anodic process (dissolution of chromium). [E.Juh.]

1063 – Investigations on the tensions of polarised anodes (in German). L. Rédey (Inst. of Inorganic Chemistry, Technical University, Budapest, Hungary). *Periodica Polytechnica*, 4 (1960) 219.

Verfasser bestimmte mit Hilfe einer eigens ausgearbeiteten Messanordnung die Polarisationsspannung von Silber- und Aluminiumanoden in Abhängigkeit von der Stromdichte. Während die mit Silber erzielten Ergebnisse mit der bekannten Polarisationsverhältnissen in jeder Hinsicht übereinstimmen, zeigten Aluminiumanoden ein anomales Verhalten. Bei diesen wurde festgestellt, dass ihre Polarisierung in Lösungen von Haloiden oder Kaliumnitrat neuartige Erscheinungen zeigt. Die als Funktion der Stromdichte aufgenommene Polarisierung verläuft einer Maximumskurve entsprechend, d.h. nach anfänglichen Verlauf in positiver Richtung neigt sie sich bei Stromdichten um 10 mA/cm² wieder zu weniger positiven Werten. Diese Erscheinung wird als ein Beweis dafür betrachtet, dass das Aluminium als Ergebnis der gemeinsamen Einwirkung des Stromes und der erwähnten Elektrolyte aktiviert wird. Die sich mit der Stromdichte parallel vergrößernden aktiven und die verbleibenden passiven Oberflächenanteile bilden eine Mischelektrode, deren resultierende Spannung gemessen werden kann. [E.Juh.]

1064 – Desalting of urine by electrodialysis. T. Wood (Biochemistry Dept., University of Sydney, New South Wales, Australia). *Nature*, 186 (1960) 634.

10 ml of urine are diluted with 10 ml of water and placed in the centre compartment of the cell and tap water is allowed to run through the electrode compartments. Current is switched on and the voltage is adjusted periodically to maintain the current flow of 0.2 A. After 43 min, the resistance of the cell rises steeply and hence the removal of ions is complete. In this study it is possible to stop the run at a time when most of the salt is removed and thus little or no amino acid is lost. [M.K.Hus.]

1065 – Oscillographic investigation of electrodeposition of chromium. H. Okada, K. Nakamura and T. Ishida (Dept. of Applied Chem., University of Osaka Prefecture, Sakai City, Osaka, Japan). *Nature*, 185 (1960) 377.

Charging curves at platinum and gold electrodes during cathodic polarisation at various current densities in a solution containing 3 M CrO₃ were measured by the oscillographic method. The graph of the charging curves at 20 A/dm² in 3 M CrO₃, 0.03 M H₂SO₄ passed through 4 inflexion points before reaching a constant potential. It is considered that in the case of Pt and Au electrodes, the initial stage of the polarisation curve corresponds to the reduction of the oxide film and a film of chromium chromate forms soon after this reduction process occurs. [M.K.Hus.]

1066 – Potentiometric studies of priming paints for metals. N. R. Bharucha (Research Association of British Paint, Colour and Varnish Manufacturers, Paint Research Station, Teddington, Great Britain). *Nature*, 187 (1960) 756.

Painted areas are generally found to be cathodic with respect to unpainted steel areas and hence a single specimen half-coated with paint may be regarded as forming a "contact couple" when immersed in a corroding environment. The tensions are recorded at regular distances from the boundary between the painted and the unpainted areas. Scanning of the specimen is effected by means of a probe calomel electrode with a KCl/agar bridge with a fine capillary tip (0.60 mm). The comparison electrode is placed at a fixed distance from the probe electrode and does not traverse the surface of the specimen. The tip of the probe electrode is kept at a distance of about 1 mm from the specimen surface. The relation between the tension and distance near the boundary between the anode and the cathode is represented by an S-shaped curve. [M.K.Hus.]

1067 – The semiconductivity of organic substances 6. A range of proteins. D. D. Eley and D. I. Spivey (Chemistry Dept., Nottingham University, Great Britain). *Trans. Faraday Soc.*, 56 (1960) 1432.

The variation of d.c. electrical conductivity with temperature has been investigated in some fourteen proteins and polypeptides in the dry state *in vacuo*. All the substances show a reproducible semiconductivity, with relatively high energy gaps, 2.6 to 3.1 eV, and high mobilities of charge carriers, 10^3 to 10^5 cm²V⁻¹sec⁻¹ assuming band theory equations and an effective mass equal to the free electron. These results confirm and extend earlier work on haemoglobin, and their outstanding feature is the overall similarity of behaviour in so many substances. The results are discussed in terms of a model in which the determining process is the penetration of a potential energy barrier by thermally excited electrons. The basic unit is regarded as the 4 π -electron $\text{>CO} \dots \text{HN}<$ unit, excited electrons travelling through a whole chain of these units of length l , with barriers between units (which might be α -keratin spirals). On the whole, the more ordered structures have lower $\Delta\varepsilon$ and higher mobility values, but the changes (*e.g.* due to denaturation) are small. Ohm's law deviations are also smaller than in other organic semiconductors. Reference is made to the correlation of thermal energy gaps with optical transitions in the solid and a solid state spectrum is reported for haemoglobin. [M.K.Hus.]

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