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LE COMPORTEMENT POLAROGRAPHIQUE DE L'ION CHROMATE

I. ÉLUCIDATION DU MÉCANISME RÉACTIONNEL ET ÉTUDE DE L'INFLUENCE DE L'ÉLECTROLYTE-SUPPORT

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(Reçu le 31 juillet 1961)

INTRODUCTION

L'ion chromate CrO_4^{2-} est la forme stable du chrome hexavalent en milieu basique, le pK de la réaction

$$CrO_4H^- \rightleftharpoons CrO_4^{2-} + H^+ \qquad (1)$$

valant 6.50, d'après NEUSS ET RIEMAN[1].

La réduction polarographique de cet anion a fait l'objet de plusieurs travaux[2-13], dont la plupart ont eu pour objet d'établir un schéma réactionnel susceptible de rendre compte de certaines anomalies caractéristiques du comportement électrochimique. LINGANE ET KOLTHOFF[2] ont montré, dans la première étude d'ensemble du système, que le polarogramme de l'ion chromate, en milieu KCl neutre et non tamponné, comprend trois ondes bien définies (A, B, C: Fig. 1, courbe 1), correspondant à la

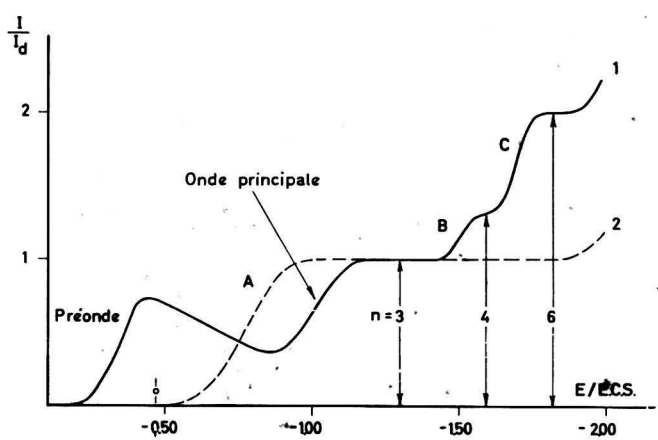

Fig. 1. Comportement polarographique de l'ion chromate 10^{-4} M, dans les milieux KCl 0.1 N (1) et NaOH 1 N (2).

* Associé au Fonds National de la Recherche Scientifique.

réduction jusqu'aux stades Cr(III), Cr(II) et Cr(O). L'onde A est précédée d'une préonde dont l'amplitude varie selon la composition, et qui affecte la forme d'un maximum arrondi, anormalement insensible à l'action des suppresseurs usuels. En milieu très basique (par exemple, milieu NaOH 1 *M*, Fig. 1, courbe 2), on observe la disparition totale de la préonde, et le recul des ondes B et C au delà de la tension de décharge des ions sodium de l'électrolyte-support.

L'étape réactionnelle Cr(VI) + 3 e → Cr(III), à laquelle se limite la présente étude, procède, en milieu neutre non tamponné* ou en milieu peu basique, selon l'équation stoechiométrique

$$CrO_4^{2-} + 4\ H_2O + 3\ e \rightarrow Cr(OH)_3 + 5\ OH^- \qquad (2)$$

En milieu suffisamment basique, il y a formation d'ions chromite selon:

$$CrO_4^{2-} + 2\ H_2O + 3\ e \rightarrow CrO_2^- + 4\ OH^- \qquad (3)$$

LINGANE ET KOLTHOFF ont suggéré que la forme particulière des polarogrammes observés en milieu neutre pourrait résulter de la formation d'un film d'hydroxyde chromique dont l'action passivante serait à l'origine du creux observé entre le maximum de la préonde et la montée de l'onde A; cette interprétation permet notamment de comprendre pourquoi l'amplitude relative du "pseudo-maximum" diminue à mesure que la concentration en chromate est augmentée (l'action passivante est en effet d'autant plus intense que les courants sont élevés en valeur absolue); elle est toutefois impuissante à expliquer les faits expérimentaux suivants:

(1) le creux subsiste à des concentrations en chromate extrêmement faibles;

(2) il s'observe à des pH relativement élevés (12–13), pour lesquels la réaction d'électrode amène la formation de l'espèce soluble non passivante CrO_2^-;

(3) la forme des oscillations de courant est absolument normale, et ne présente pas les irrégularités typiques qui accompagnent les réactions perturbées par la formation d'un dépôt superficiel non conducteur.

Ce n'est en fait qu'à des concentrations en chromate assez élevées, et dans un domaine de pH assez limité (inférieur à env. 11) que l'on peut déceler un comportement passivé**.

Examinant en détail l'influence du pH et de la hauteur du réservoir, GREEN ET WALKLEY[7] arrivent à la conclusion que la préonde est d'origine cinétique, et qu'elle correspond à la réaction chimique antécédente

$$CrO_4^{2-} + H^+ \rightarrow HCrO_4^-$$

produisant l'ion chromate acide qui serait seul réductible aux potentiels considérés. Selon la composition, H_2O ou HCO_3^- constituerait le donneur de protons. Les auteurs signalent les caractéristiques assez particulières du maximum, et suggèrent la possibilité d'un mécanisme entièrement différent, influencé par la double-couche électrochimique et analogue à celui observé lors de la réduction d'ions tels que $S_2O_8^{2-}$ et $Fe(CN)_6^{3-}$.

* Il y a dans ce cas élévation locale du pH par suite de la formation d'ions hydroxyle par l'électrolyse.

** Il en est autrement pour l'onde B, plus aisément perturbée par la formation de $Cr(OH)_2$.

Par ailleurs, DELAHAY[5] a suggéré qu'une réaction électrochimique amenant la formation de chrome tétravalent pourrait expliquer certaines anomalies observées dans la forme des courbes de polarisation.

Réexaminant indépendamment le problème[11,12], nous avons montré que la position de l'onde principale A est absolument indépendante du pH, mais varie par contre considérablement avec la concentration de l'électrolyte-support.

Le fait que l'influence du pH est nulle peut être illustré, à titre d'exemple, par la constatation que l'on mesure pratiquement la même tension de demi-onde (soit —0.78 V/E.C.S.) dans les milieux respectivement NaOH M, NaOH 0.1 M + $NaClO_4$ 0.9 M, et NaOH 0.01 M + $NaClO_4$ 0.99 M). On peut déduire de ce comportement que l'étape irréversible est constituée par la réduction directe de l'ion chromate, par transfert électronique lent, selon:

$$CrO_4^{2-} + ne \longrightarrow \qquad (4)$$

(mettant probablement en jeu un électron, et à l'intervention éventuelle de molécules d'eau).

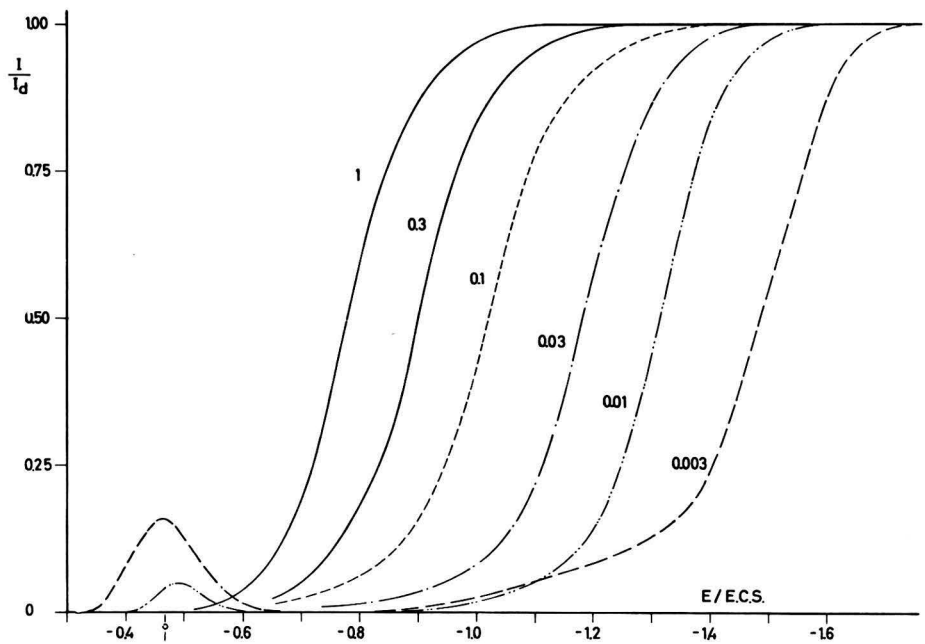

Fig. 2. Comportement polarographique de l'ion chromate $2 \cdot 10^{-4}$ M, en milieu NaOH (les chiffres expriment les diverses valeurs de [NaOH] en mol/(e).

Par ailleurs, l'influence de la force ionique est illustrée à la Fig. 2 (milieu NaOH): la vitesse réactionnelle est d'autant plus faible que la concentration de l'électrolyte-support est abaissée. Lorsque la force ionique est inférieure à environ 0.001, l'onde tend à se confondre dans la seconde onde de réduction (onde B)*.

* Cette seconde onde s'observe pour des pH inférieurs à environ 13.5; elle présente un courant-limite mal défini, dont l'amplitude varie avec la composition (elle est au maximum égale à celle

Ce comportement peut être expliqué quantitativement à partir de la théorie de FRUMKIN[14,15,16], qui corrige la théorie du transfert électronique lent de VOLMER[17], en y introduisant des facteurs représentatifs de la perturbation causée par la présence de la double-couche électrochimique.

Dans le cas d'un processus de réduction totalement irréversible, la constante de vitesse expérimentale observée à un potentiel donné φ est donnée par la relation:

$$v_\varphi = k_0 \exp \frac{\alpha n_\alpha F}{RT} \left[-\varphi - \left(\frac{z_A}{\alpha n_\alpha} - 1 \right) \psi_\delta^* \right] \tag{5}$$

Dans cette relation:

v_φ est la constante de vitesse "apparente" calculée en négligeant l'influence de la double-couche électrochimique, en cm sec^{-1};

k_0 est la constante de vitesse "vraie" observée au point zéro de l'échelle rationnelle de GRAHAME (soit —0.47 V/E.C.S.) en cm sec^{-1};

α est le coefficient de transfert;

n_α le nombre d'électrons impliqués dans l'étape déterminante;

φ est la tension d'électrode dans l'échelle rationnelle de GRAHAME (toute autre tension de référence pourrait être adoptée);

z_A est la charge de la particule dépolarisante (+1 dans le cas d'un cation monovalent);

et ψ_δ^* est le potentiel ψ règnant à la distance δ^* (comptée à partir de la surface de l'électrode) où se trouve le centre électrique de la particule dépolarisante au moment de l'acte réactionnel.

Si la structure de la double-couche est déterminée par la présence d'un excès d'électrolyte-indifférent, on peut admettre que ψ_δ^* est également la distance correspondant au plan externe de HELMHOLTZ. Il est dès lors possible — du moins dans certains cas favorables — de calculer ψ_δ en fonction de la tension appliquée et de la composition. On peut ainsi, en principe, interpréter l'influence du milieu sur la morphologie des courbes de polarisation, et calculer les paramètres cinétiques vrais de la réaction d'électrode considérée. Une telle méthode a été pour la première fois appliquée par FRUMKIN[14] à l'étude de la cinétique de décharge des protons sur le mercure. Nous l'avons récemment utilisée[18] pour expliquer le comportement polarographique du système

$$Eu^{3+} + e \rightleftharpoons Eu^{2+}$$

La validité de la relation (5) est subordonnée à diverses conditions, parmi lesquelles: (1) la particule dépolarisante ne doit pas être spécifiquement adsorbée; (2) sa concentration dans la partie diffuse de la double-couche doit être déterminée exclusivement par l'action de forces électrostatiques, à l'exclusion de termes représentatifs du travail de polarisabilité; (3) les conditions locales prévalant dans la partie diffuse doivent satisfaire au modèle de GOUY–CHAPMAN.

L'évaluation de ψ_δ présente par ailleurs certaines difficultés, si un ou plusieurs anions de l'électrolyte-support sont spécifiquement adsorbés.

De manière à apprécier dans quelle mesure la relation (5) est susceptible de décrire

de la première onde, ce qui correspondrait à l'électro-déposition de chrome métallique), et qui est fréquemment déformé vers —1.85 V par un creux, vraisemblablement causé par le blocage de la surface par un film d'hydroxyde chromeux. Ces circonstances défavorables compliquent considérablement l'étude cinétique du processus, et en limitent l'intérêt.

les courbes polarographiques de la Fig. 2, la méthode graphique suivante a été utilisée: on choisit une constante de vitesse arbitraire (dans l'exemple choisi, celle qui correspond aux tensions de demi-onde, soit env. $1.25 \cdot 10^{-3}$ cm sec^{-1}), et on détermine les valeurs de ces tensions pour les diverses forces ioniques. On calcule ensuite les valeurs de ψ_δ correspondantes à l'aide de la théorie de GOUY–CHAPMAN (en utilisant les valeurs de densité de charge superficielle données par GRAHAME[27] pour des solutions de NaF à diverses concentrations, et en interpolant si nécessaire). On établit enfin un diagramme ayant ψ_δ pour ordonnée et $E_{\frac{1}{2}}$ pour abscisse (Fig. 3). Si la relation

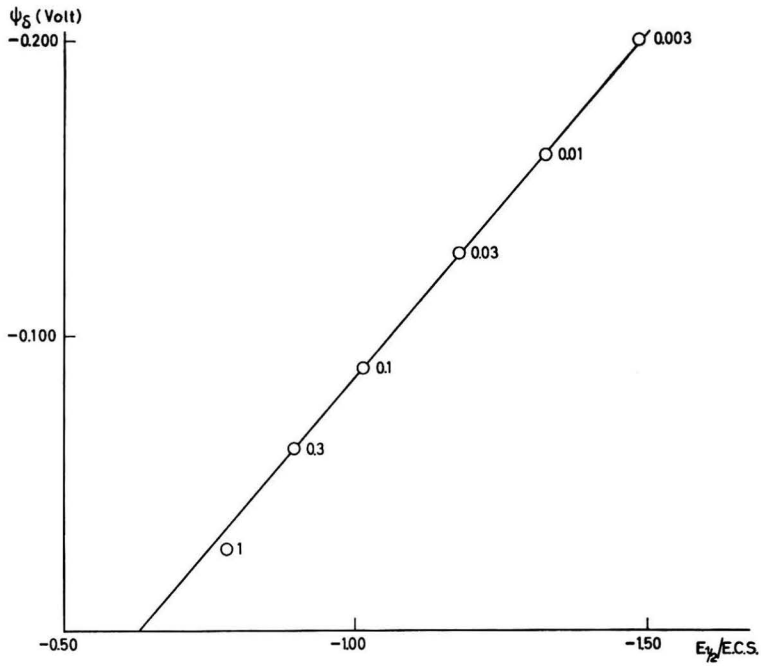

Fig. 3. Relation entre $E_{\frac{1}{2}}$ et les valeurs correspondantes du potentiel ψ_δ, en fonction de la concentration en NaOH (exprimée en mol/l).

(5) est vérifiée, les points expérimentaux doivent s'aligner sur une droite, dont la pente vaut $[z_A/\alpha n_\alpha) - 1]^{-1}$ et dont l'intersection avec l'abscisse donne la valeur de $E_{\frac{1}{2}}$ que l'on observerait en l'absence de double-couche: ces données numériques permettent la détermination des paramètres αn_α et k_0 (respectivement évalués à 0.60 et $3 \cdot 10^{-5}$ cm sec^{-1}), à partir desquels les diverses fonctions constante de vitesse–tension peuvent être finalement recalculées et comparées aux valeurs expérimentales, elles-mêmes établies en recourant à la méthode de MEJMAN–KOUTECKY[19,20].

L'examen des Figs. 3 et 4 mène à la conclusion que le comportement observé est en accord remarquable avec les prévisions basées sur la théorie de FRUMKIN, dans tout le registre des tensions et des forces ioniques*. Cette circonstance extrêmement

* L'origine des déviations observées pour les milieux 0.3 M et 1 M sera discutée plus loin, à la lumière de l'étude du comportement de l'ion chromate plus fortement concentré (courbe en traits d'axe).

favorable permet en principe — sous réserve de la validité de la relation (5) — de calculer, par extrapolation, les valeurs des constantes de vitesse au voisinage et en deçà du point de charge nulle, et d'apprécier ainsi dans quelle mesure la préonde ne pourrait être due au même mécanisme que celui qui détermine l'onde principale.

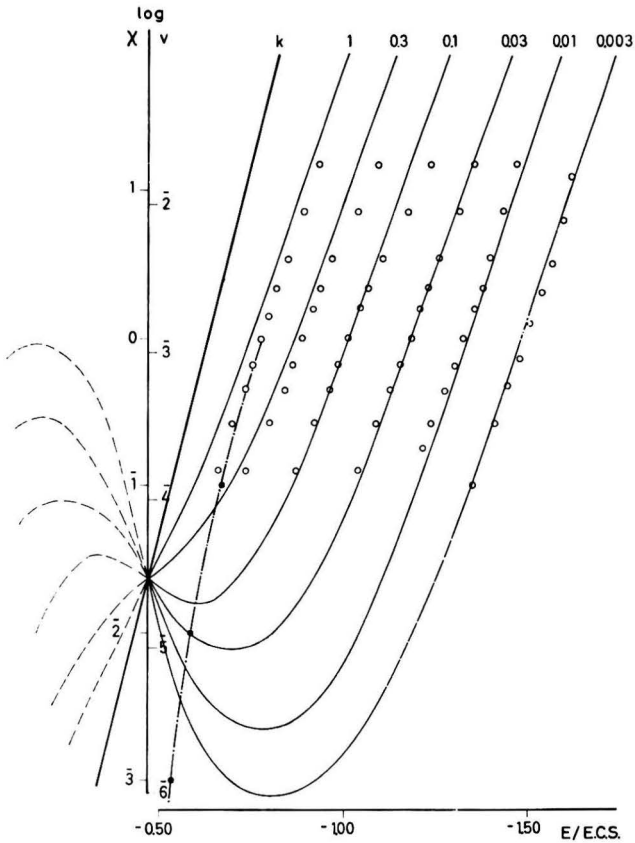

Fig. 4. Vérification de la relation de FRUMKIN. Les courbes en traits pleins ont été calculées sur la base des valeurs $\alpha n_\alpha = 0.60$ et $\log k_0 = \bar{5}.48$. Les cercles blancs représentent les valeurs expérimentales obtenues en milieu NaOH (conc. expr. en mol/l). La conc. en chromate était $2 \cdot 10^{-4}$ M/l, sauf pour la courbe en traits d'axe (voir texte).

Une telle hypothèse a été récemment admise par DELAHAY[13], qui interprète le comportement observé à l'électrode d'amalgame de thallium en termes d'un mécanisme unique (transfert électronique lent), analogue à celui proposé par FRUMKIN pour rendre compte du comportement de l'ion persulfate. En fait, cette hypothèse de travail n'est, dans le cas du mercure du moins, qu'en accord très médiocre avec l'expérience, si l'on tente de comparer les courbes polarographiques observées en milieu dilué, avec les fonctions vitesse–potentiel correspondantes, extrapolées en deçà du point de charge nulle (Fig. 4 — courbes en traits interrompus). En outre, l'influence du pH est difficilement explicable, sinon en assignant à l'ion hydroxyle un pouvoir superficiel anormalement élevé.

Ces considérations nous ont amené[11,12] à adopter l'hypothèse de GREEN ET WALKLEY, en l'aménageant de manière à tenir compte du fait que le courant cinétique est perturbé par la présence de la double-couche. Ce point de vue permet d'expliquer de manière relativement satisfaisante l'influence du pH et de la force ionique, et la morphologie particulière de la préonde. Toutefois, certaines expériences indiquent que le pH est loin d'être le seul facteur déterminant: son influence semble anormalement faible pour certains milieux (Na_2CO_3 notamment, voir Fig. 10). A même pH, l'amplitude de la préonde dépend considérablement de la composition, même à force ionique égale (voir Fig. 23). En outre, la morphologie en "maximum" subsiste à des forces ioniques telles que l'influence de la double couche devrait être totalement négligeable.

L'existence de ces anomalies conduit à reconsidérer le problème de la nature de l'étape déterminante, d'autant plus que la nécessité nous est apparue de tenir compte de deux autres éléments d'appréciation importants:

(1) La tension d'équilibre de la réaction

$$CrO_4^{2-} + 2\,H_2O + 3\,e \rightleftharpoons CrO_2^- + 4\,OH^- \qquad (6)$$

vaut, sur la base des données thermodynamiques de LATIMER

$$E_{(25°)} = -0.42\ V - 0.079 \log [OH^-] \qquad (7)$$

On peut en déduire que la préonde se développe à des tensions relativement peu éloignées des valeurs de la tension d'équilibre: dans de telles conditions, la réaction d'électrode peut cesser d'être totalement irréversible, et la contribution au courant due au processus d'oxydation ne peut être a priori négligée. Ce fait pourrait expliquer pourquoi la préonde ne se développe pas à des tensions aussi positives que celles que laissent prévoir les courbes extrapolées de la Fig. 4: un des arguments en défaveur d'un mécanisme par décharge directe se trouve ainsi éliminé.

(2) L'ion chromate est appréciablement tensioactif, dans le domaine des tensions considérées: des mesures de cadence de chute effectuées à l'aide d'une électrode à gouttes de mercure dans le domaine relativement étroit des tensions où l'électrode peut être considérée comme idéalement polarisable (Fig. 5) nous ont montré que l'activité superficielle de l'ion chromate se situe entre celle des ions Cl^- et Br^-. Une preuve indirecte de l'adsorption spécifique est fournie par la position de l'onde de réduction de l'ion persulfate en utilisant Na_2CrO_4 comme électrolyte-support. En milieu $M/2$, la tension de demi-onde est de l'ordre de —0.25 V/E.C.S., ce qui correspond à un ralentissement important, dont l'origine doit être attribuée au renversement de la charge de la partie diffuse de la double-couche, résultant de la présence des ions chromate. L'adsorption spécifique des ions chromate reste notable au voisinage du point d'i charge nulle: il doit évidemment être tenu compte de ce fait lors de l'élucidation de mécanisme déterminant, dont le problème de l'identification reste ainsi posé.

Les considérations qui viennent d'être développées permettent de définir le double objet de la présente communication:

(1) Le fait que l'onde principale est assez fidèlement décrite par la relation (5) rend possible d'en subordonner l'étude à celle de la structure fine de la double-couche. A cet effet, il est intéressant de reconnaître de manière systématique l'influence de la composition de l'électrolyte-support, et d'évaluer dans quelle mesure les effets observés peuvent être interprétés en termes d'une modification de la structure de l'inter-

phase et de son profil potentiel–distance. On examinera successivement l'influence de la nature et de la concentration des principaux cations alcalins (Li^+, Na^+, K^+, Cs^+) et de divers ions ammonium quaternaire (cette étude étant exposée dans la seconde

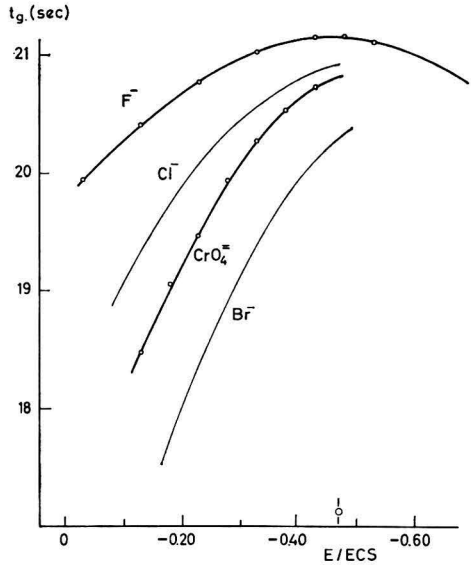

Fig. 5. Comportement électrocapillaire de l'ion chromate (évalué par la mesure de la période de chute t_g d'une électrode à goutte de mercure) comparé à celui des ions Cl^- et Br^-. Les diverses solutions sont 0.9 N (soit 0.45 M pour le chromate).

partie de cette communication, publiée séparément). Le rôle de l'anion sera également reconnu, à l'aide d'expériences comparatives utilisant divers sels d'un même cation donné. Le cas mixte où la solution contient simultanément un cation et un anion tensioactif sera enfin brièvement considéré.

(2) Par ailleurs, le problème de la nature de la préonde sera réexaminé, en tenant compte, notamment, de facteurs discutés plus haut. Une fois le mécanisme reconnu (à l'aide d'expériences où la composition sera établie de manière à simplifier au maximum la structure interfaciale) il est en principe possible d'étudier l'influence de l'adsorption spécifique (cationique, anionique et mixte): de telles expériences seront à la fois susceptibles de confirmer le mécanisme proposé, et d'apporter des éléments nouveaux à la compréhension de la structure fine de la double-couche, dans le domaine des tensions voisines du point de charge nulle.

APPAREILLAGE ET RÉACTIFS

Les courbes polarographiques ont été établies en utilisant les valeurs du courant instantané maximum, mesurées à l'aide d'un polarographe de conception classique, équipé d'un millivoltmètre BROWN, type 153X12 V, monté en microampèremètre à sensibilité variable et fonctionnant sans circuit d'amortissement. La composante capacitive des courants a été défalquée graphiquement, à partir des polarogrammes de l'électrolyte-support seul.

La tension, appliquée entre l'électrode à gouttes et une nappe de mercure, était fournie par un potentiomètre (100 Ω, deux spires par millivolt), entraîné par un moteur synchrone; la vitesse de variation de la tension n'était jamais supérieure à 5 cV par minute, sauf pour le tracé des polarogrammes destinés à contrôler la constance du courant de diffusion, avant et après le relevé des courbes étalées. La tension imposée à l'électrode à gouttes était mesurée à $\pm$ 2 mV, par rapport à une électrode au calomel saturé (connectée à la cellule par un siphon semi-capillaire contenant la solution étudiée), en utilisant un potentiomètre électronique à haute impédance d'entrée.

L'électrode à gouttes était constituée par un capillaire cylindrique en verre Iéna, long d'environ 25 cm, assurant un débit de mercure de l'ordre de 0.85 mg sec^{-1}, pour une hauteur d'environ 1 m, avec une période de chute spontanée dans l'eau distillée supérieure à 10 sec. La période était maintenue à 4.00 sec, en utilisant un marteau-frappeur électromagnétique, commandé par un générateur d'impulsions synchronisé sur la fréquence du réseau d'alimentation secteur.

Toutes les expériences ont été effectuées à 25.0° $\pm$ 0.1°. Les solutions étaient désoxygénées en y insufflant de l'azote pur finement divisé, garanti à moins de 0.0005% d'oxygène.

Les diverses solutions ont été préparées à partir d'eau tridistillée; les distillations étaient conduites de manière discontinue, de manière à permettre le rejet systématique des fractions de tête, qui pourraient être susceptibles de contenir des matières organiques volatiles, non oxydables par le permanganate de potassium.

Le mercure était purifié par une double distillation sous vide, précédée d'une oxydation par barbotage d'air, effectuée sous acide nitrique dilué.

La solution-mère de chromate de sodium a été préparée par pesée exacte d'une prise de sel "Merck" pro analysi, préalablement recristallisé et séché à l'étuve.

Les électrolytes-supports LiOH, NaOH et KOH ont été préparés par dissolution directe, en prenant les précautions usuelles pour éviter la carbonatation, et titrés par acidimétrie. CsOH a été préparé électrolytiquement à partir de CsCl, à l'aide d'une cellule à nappe de mercure compartimentée. Les solutions de fluorure, chlorure, bromure, sulfate et phosphate de sodium ont été préparées par pesée exacte à partir de sels amenés à composition définie, par desséchage jusqu'à poids constant, effectué à des températures choisies en fonction des données thermodynamiques de DUVAL[21]. Les solutions d'iodure et de thiocyanate ont été titrées par argentométrie.

MÉTHODES DE CALCUL

L'analyse cinétique des courbes polarographiques a été effectuée en utilisant les méthodes de MEJMAN[19] et de KOUTECKY[20], basées sur la détermination du paramètre sans dimension χ, dont il existe des valeurs tabulées en fonction de l'amplitude relative I/I_d du courant instantané maximum[20].

Dans le cas d'une réaction de décharge directe totalement irréversible, on a :

$$v = \chi \sqrt{\frac{7 D_0}{12 tg}} \tag{8}$$

où v est la constante de vitesse *apparente* en cm sec^{-1};
D_0 le coefficient de diffusion en cm^2 sec^{-1};
tg la période de chute (soit ici 4.00 sec).

Dans le cas où le courant est totalement contrôlé par une réaction chimique volumique du type

$$A \rightarrow B + Z \tag{9}$$

(A étant la forme prépondérante de l'espèce dépolarisante, et B sa forme électroactive), on a[20]

$$\vec{r} = \frac{7}{12} \frac{[Z]}{K\,tg} \chi^2 \tag{10}$$

où $\vec{r}$ est la constante de vitesse apparente de transformation de A en sec^{-1}; et K la constante d'équilibre de la réaction en $mol.cm^{-3}$.

Les quantités v et $\vec{r}$ sont dites "apparentes", car elles incluent implicitement un terme représentatif de l'influence de la double-couche électrochimique. La relation entre v et k (constante cinétique vraie) est donnée par l'équation (5). L'étude de la relation liant $\vec{r}$ à $\vec{r_0}$ (constante cinétique réelle du processus (9)) a fait l'objet de travaux récents (GIERST ET HURWITZ[22], MATSUDA[23], HURWITZ[24]).

Les potentiels ψ_δ dont il est fait usage ont été calculés à partir de la relation charge–potentiel de GOUY–CHAPMAN[25,26] en considérant que la densité de charge de la partie diffuse de la double couche est égale à celle de l'électrode, au signe près. Les valeurs de densité de charge superficielle utilisées sont celles établies par GRAHAME[27] (milieux NaF 0.92; 0.66; 0.10; 0.01 et 0.001 N), en recourant à l'interpolation pour les concentrations intermédiaires. L'applicabilité d'un tel calcul est limitée au cas des solutions sodiques, dans le domaine des tensions correspondant à la branche négative de la courbe électrocapillaire (et éventuellement à partir de plusieurs décivolts au delà du point de charge nulle, s'il y a adsorption spécifique anionique importante). De toute manière, ces potentiels doivent être considérés comme de simples ordres de grandeur, étant donné que l'adsorption spécifique des ions sodium est tenue pour négligeable (ce qui n'est vrai qu'en première approximation) et que certaines simplifications excessives sont implicites dans la théorie de GOUY–CHAPMAN[25,26]. Les tensions d'électrode E sont exprimées par rapport à l'électrode au calomel saturé.

PARTIE EXPÉRIMENTALE ET DISCUSSION

On considérera séparément les caractéristiques de l'onde principale et celles de la préonde. L'onde principale sera étudiée en premier lieu, car certaines de ses propriétés constituent des éléments utiles à l'élucidation du mécanisme déterminant de la préonde.

L'Onde Principale

Ses caractéristiques essentielles on été établies antérieurement[11,12], et ont été résumées dans la partie introductive. De manière à simplifier l'interprétation de l'influence de la composition, on a utilisé deux séries d'électrolytes-supports, ne variant que par la nature du cation ou de l'anion, l'autre ion commun étant choisi en fonction de son absence d'activité électrocapillaire. Cette condition nous a amené à choisir la série des hydroxydes alcalins, et celle des sels de sodium.

A. Influence de la nature et de la concentration du cation-support sur les caractéristiques de l'onde principale

Le nombre des cations utilisables est sévèrement limité par la nécessité d'opérer en milieu basique et en présence d'ions chromate. Ce fait limite pratiquement le choix aux seuls ions des métaux alcalins. (Le cas des ions ammonium quaternaire sera traité dans une communication séparée, celui des ions magnésium sera considéré lors de l'étude de la préonde.) De manière à atténuer au maximum l'importance de la préonde, dont l'amplitude diminue à pH croissant, on a opéré en milieu hydroxyde. Ce milieu présente l'avantage supplémentaire d'une bonne conductivité électrique, ce qui permet d'annuler la composante de migration de l'ion chromate pour des excès en électrolyte-support relativement faibles: l'étude des milieux dilués s'en trouve ainsi facilitée.

Les courbes polarographiques de l'ion chromate $2 \cdot 10^{-4}$ *M* ont été relevées dans les milieux LiOH, NaOH, KOH et CsOH aux molarités 1, 0.3, 0.1, 0.03, 0.01 et 0.003.

Les Figs. 2 et 6 illustrent les comportements observés dans les milieux NaOH et CsOH, choisis à titre d'exemple.

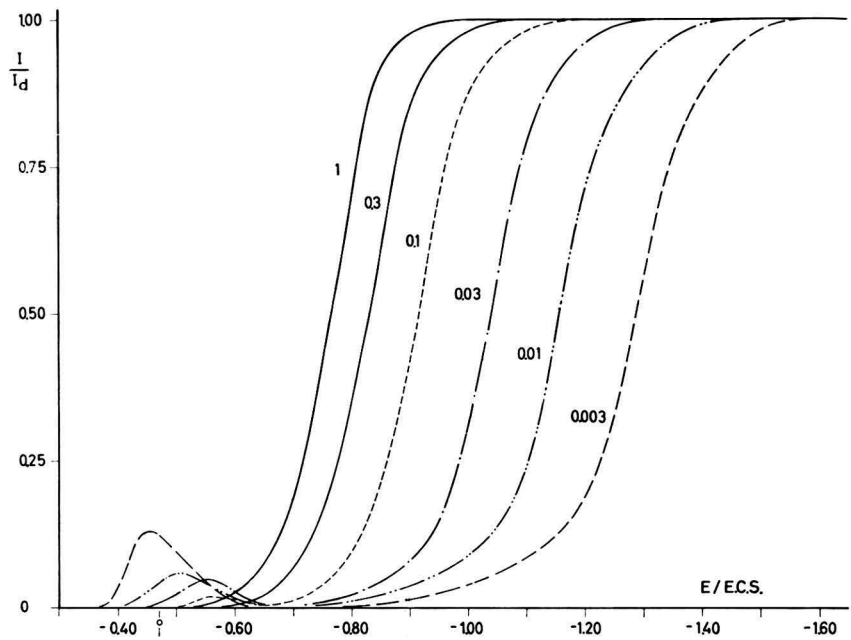

Fig. 6. Comportement polarographique de l'ion chromate $2 \cdot 10^{-4}$ *M*, en milieu CsOH (les chiffres expriment les diverses valeurs de [CsOH] en mol/l).

L'examen d'ensemble des familles de courbes obtenues permet de tirer les conclusions suivantes:

(1) La valeur du courant-limite dépend peu de la composition. Les diverses valeurs du coefficient de diffusion de l'ion chromate (Tableau I), calculées à partir de l'équation d'ILKOVIC, varient peu, autour d'une valeur moyenne de l'ordre de $1.08 \cdot 10^{-5}$ cm^2 sec^{-1}. C'est cette valeur qui a été utilisée dans le calcul des constantes de vitesse.

TABLEAU I

INFLUENCE DE L'ÉLECTROLYTE-SUPPORT SUR LE COEFFICIENT DE DIFFUSION DE L'ION CHROMATE

Concentration (M)	$D_0 \cdot 10^5 (cm^2\ sec^{-1})$			
	LiOH	*NaOH*	*KOH*	*CsOH*
1	0.94	1.00	1.09	1.00
0.3	0.99	1.04	1.09	1.03
0.1	1.01	1.08	1.09	1.12
0.03	1.06	1.10	1.11	1.12
0.01	1.05	1.09	1.13	1.12

En accord avec le fait qu'il s'agit d'un courant de diffusion, l'amplitude du courant-limite a été trouvée proportionnelle à la concentration en chromate, dans le registre des concentrations inférieures à 10^{-3} *M*. Pour des concentrations plus fortes, et à des pH relativement peu élevés, les ondes tendent à devenir irrégulières et mal définies, vraisemblablement par suite de la formation d'un film d'hydroxyde chromique doué de propriétés passivantes.

(2) Les ondes se déplacent régulièrement vers les tensions négatives à mesure que l'on diminue la force ionique, l'effet de la concentration étant prépondérant sur celui de la nature des ions. A la seule exception des milieux NaOH et LiOH 1 *M*, où l'on observe une certaine déformation, les ondes sont extrêmement régulières, malgré l'absence de suppresseur de maximum.

(3) A même concentration, la position des ondes dépend quelque peu de la nature du cation, l'effet étant maximum aux forces ioniques faibles (auxquelles correspondent des tensions très négatives). De manière à permettre d'apprécier l'influence du cation, on a porté les diverses valeurs des tensions de demi-onde (auxquelles correspondent une constante de vitesse apparente de l'ordre de $1.25 \cdot 10^{-3}$ cm^2 sec^{-1}) en fonction de la concentration des divers cations considérés (Fig. 7). On constate que la réaction

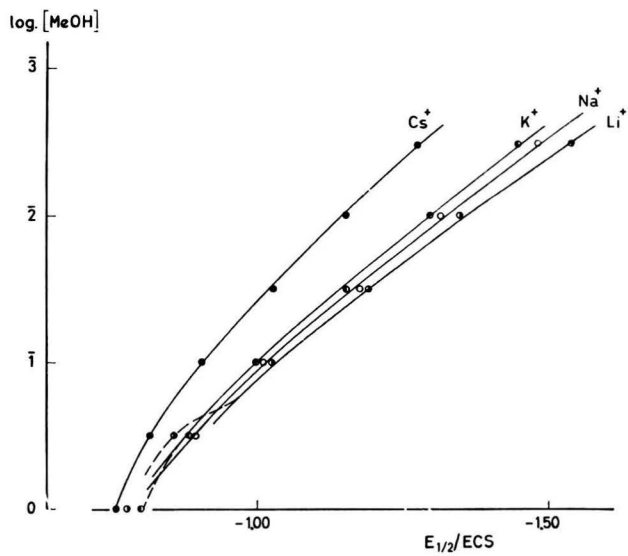

Fig. 7. Influence de la nature et de la concentration du cation-support sur les valeurs de la tension de demi-onde.

est accélérée lorsque l'on passe de Li^+ à Cs^+, l'effet étant particulièrement notable pour l'ion césium. Par ailleurs, l'amplitude de l'accélération décroît à mesure que l'on augmente la force ionique (ce qui rend la tension d'électrode moins négative). En milieu molaire, on remarque des inversions dans l'ordre des tensions de demi-onde, liées aux déformations signalées plus haut.

Discussion. (1) Le fait que l'influence de la nature du cation est d'autant plus importante que sa concentration est abaissée permet d'éliminer tout mécanisme basé sur l'hypothèse d'une action directe sur les paramètres cinétiques de la fonction constante de vitesse vraie.

(2) Par contre, le parallélisme entre le comportement observé et celui présenté par d'autres systèmes (parmi lesquels: réduction de l'ion persulfate[15,28], et celles de l'ion zinc[29] et de l'ion nickel[30] où le sens de l'effet inverse), joint au fait que les capacités d'électrode croissent à mesure que l'on se déplace dans la série vers l'ion Cs^+, mène à la conclusion que l'effet déterminant est causé par une modification structurale de la double-couche. A cet égard, on peut considérer les possibilités suivantes, qui seront brièvement analysées:

(a) la distance de moindre approche du cation-support dépend de sa nature;

(b) le potentiel ψ_δ est d'autant plus abaissé que la polarisabilité du cation-support est grande;

(c) il y a adsorption spécifique, d'importance variable selon le cation-support.

(a) La première hypothèse est en accord avec les conceptions de GRAHAME. La diminution de la distance de moindre approche a pour effet d'augmenter la capacité d'électrode, et par voie de conséquence les valeurs de la densité de charge et celles des potentiels ψ_δ. L'effet cinétique correspondant à une diminution du potentiel ψ_δ^*, il est nécessaire d'admettre que la distance de moindre approche de l'ion chromate est suffisamment différente pour surcompenser l'accroissement de ψ_δ. Ainsi que l'a montré FRUMKIN, cette hypothèse est inconciliable avec le fait que les différences de comportement subsistent à la tension correspondant au point de charge nulle. En parallèle avec certaines expériences de cet auteur[31], nous avons trouvé que l'influence cationique sur la préonde reste significative, même à des tensions appréciablement plus positives que celles du maximum électrocapillaire.

(b) On sait que les particules polarisables tendent à s'accumuler dans les régions où règne un champ électrique, le travail associé à leur déformation étant proportionnel au carré du champ local. Cet effet, négligé dans les traitements simplifiés de GOUY–CHAPMAN ET STERN a été considéré récemment avec quelque détail[32]. Il apparaît qu'à densité de charge égale, les potentiels ψ_δ sont d'autant inférieurs à la valeur tirée de l'équation non corrigée que la polarisabilité du cation-support est élevée. On remarquera que cet effet, dont il est difficile d'évaluer quantitativement l'importance, devrait également s'annuler à la tension du maximum électro-capillaire (adsorption anionique exclue), pour laquelle le champ électrique est théoriquement nul en tout point de la partie diffuse.

(c) L'hypothèse d'une adsorption spécifique croissante dans la série Li^+–Cs^+ [31], proposée par FRUMKIN, a l'avantage d'être la seule à être susceptible d'interpréter le comportement aux environs du point de charge nulle. A cet égard, le comportement de l'ion césium est analogue à celui d'autres cations, tels que Tl^+ et Pb^{2+}.

Il est probable que le taux variable de l'adsorption spécifique selon la nature du cation-support joue le rôle principal dans le comportement de l'ion chromate. Toute-

fois, la possibilité d'une coopération avec les mécanismes précédemment considérés (et principalement le second) ne peut être exclue a priori. Si l'on admet que l'adsorption spécifique est exclusivement déterminante, il est possible, sur la base des valeurs de densité de charge superficielle, calculées par GRAHAME[33] (uniquement limitées aux milieux 0.1 M) et de nos résultats expérimentaux, d'évaluer la quantité d'ions Cs^+ spécifiquement adsorbés, si l'on admet que l'adsorption de l'ion sodium est comparativement négligeable.

Choisissons, par exemple, la tension arbitraire de —0.97 V/E.C.S., à laquelle les courants polarographiques de réduction de l'ion chromate ont une amplitude satisfaisante dans les milieux NaOH et CsOH. On calcule qu'à cette tension, la constante cinétique apparente est environ 6.7 fois supérieure en milieu césium. Si l'on admet que les constantes cinétiques apparentes ne dépendent, à tension d'électrode donnée, que de la valeur de ψ_δ selon la relation:

$$\Delta \ln v = \frac{(z_A - \alpha n_\alpha) F}{RT} \Delta\psi_\delta \qquad (11)$$

que l'on tire aisément de (5), on calcule que le remplacement des ions Na^+ par les ions Cs^+ amène une variation $\Delta\psi_\delta$ de l'ordre de 19 mV. En milieu NaOH, ψ_δ vaut environ —86 mV; cette valeur tombe ainsi à —67 mV en milieu CsOH. On calcule ensuite que la charge de la partie diffuse vaut +6.25 μcoulombs cm^{-2} en milieu CsOH. La densité de charge superficielle étant, selon GRAHAME, de 10.6 μcoulombs cm^{-2}, on peut en conclure qu'environ 4.35 μcoulombs cm^{-2}, soit un peu moins de la moitié des ions Cs^+ en excès, sont spécifiquement adsorbés. Une telle adsorption, quoique significative, n'amène donc pas un renversement de la charge de la partie diffuse, à l'inverse de ce qui peut s'observer dans le cas d'anions très tensioactifs, à des tensions suffisamment positives.

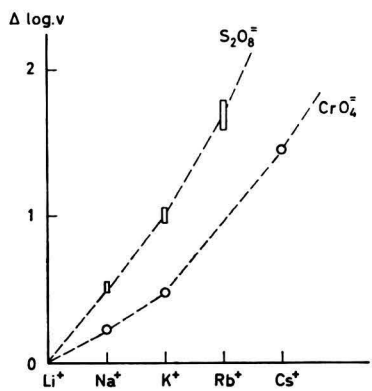

Fig. 8. Variation relative des constantes de vitesse apparentes de réduction des ions chromate et persulfate, en fonction de la nature du cation-support (0.01 M).

(3) Il n'est pas sans intérêt de comparer le comportement de l'ion chromate à celui de l'ion persulfate. Dans le domaine des tensions négatives par rapport au point de charge nulle, et à des forces ioniques suffisamment faibles, les courbes polarographiques de l'ion persulfate présentent en effet un creux caractéristique, dont l'étude

détaillée a été effectuée par LOSKAREV, FRUMKIN et ses collaborateurs[28]. En particulier, NIKOLAJEWA, DAMASKIN ET AKOPJAN (ref.[15] p. 811) ont reconnu l'influence de la nature du cation sur la morphologie des courbes de polarisation: il est ainsi possible, à partir d'un graphique établi par ces auteurs, de comparer les ions CrO_4^{2-} et $S_2O_8^{2-}$ dans les mêmes circonstances de tension et de composition (si l'on excepte la nature de l'anion-support, qui joue un rôle totalement négligeable aux tensions considérées).

Le graphique de la Fig. 8 schématise l'influence spécifique des divers cations à —0.85 V/E.C.S. et en milieu 0.01 M. La quantité portée en ordonnée est le logarithme du rapport des vitesses, en adoptant la valeur trouvée en milieu lithium comme niveau de référence. On remarque que l'influence spécifique est notablement plus marquée dans le cas de l'ion persulfate, pour lequel αn_α est cependant plus petit. Par ailleurs, les variations observées pour l'ion chromate sont approximativement parallèles aux variations correspondantes de la densité de charge superficielle (peu différentes pour Li^+, Na^+ et K^+, très grande pour Cs^+). Ces constatations nous ont amené[11,12] à considérer que le comportement de l'ion chromate était le plus proche de la normale, mais que, par contre, il pouvait exister une interaction persulfate-cation, amenant la formation locale d'une entité plus ou moins associée, de type $S_2O_8Me^-$, caractérisée par une constante de vitesse de formation variant avec la nature du partenaire cationique. Il n'apparaît toutefois pas impossible que ce soit le comportement de l'ion persulfate qui puisse être tenu pour normal, et que l'effet spécifique plus faible observé avec l'ion chromate résulte du fait que cet ion, relativement polarisable, est soumis à un effet concentrateur dû au champ électrique local, qui contrebalance dans une certaine mesure l'effet de répulsion électrostatique, et atténue ainsi l'influence spécifique du cation-support. Cette éventualité, qui ne peut être écartée a priori, conduirait à remettre en question l'applicabilité de la relation (5) au cas du chromate et la validité des méthodes de calcul utilisées pour la détermination des paramètres αn_α et k_0, qui seraient ainsi encore dépendants de facteurs étrangers à la réaction de transfert électronique proprement dite. A en juger par le fait que la relation de FRUMKIN reste vérifiée dans un large registre de potentiels et de concentrations, on peut présumer que l'erreur ainsi commise est pratiquement négligeable.

(4) Aux forces ioniques élevées, on observe que les courbes polarographiques sont légèrement déplacées dans le sens des tensions négatives, par rapport à la position qu'elles devraient théoriquement occuper, sur la base de la relation (5) avec les valeurs de αn_α et k_0 établies de manière à rendre compte au mieux de l'ensemble des diverses courbes. Quoique cet écart puisse trouver son origine dans le fait que le milieu s'écarte notablement de l'idéalité (modèle de double-couche insuffisamment approché, variation de la vitesse vraie avec la force ionique, etc.), il nous a paru utile d'examiner plus en détail s'il ne pouvait s'agir d'une déviation à la relation de VOLMER de la fonction liant la constante de vitesse vraie au potentiel. De manière à pouvoir mesurer des constantes de vitesse inférieures à 10^{-5} cm sec^{-1} sans être gêné par l'interférence du courant capacitif, une série d'expériences ont été effectuées, en augmentant graduellement la concentration en chromate de $2 \cdot 10^{-4}$ à 0.1 M, et en maintenant la force ionique constante (à la valeur 1) par addition complémentaire d'hydroxyde de potassium.

En opérant à sensibilité constante, et en évaluant les divers courants de diffusion par extrapolation, il est possible d'étendre considérablement le domaine des constantes de vitesse accessibles (Fig. 4, courbe en traits d'axe —·—·—·). Ces expériences

ont montré que la pente d $\log \chi/dE$ augmente de manière anormalement élevée lorsque la surtension est abaissée, l'effet devenant nettement décelable en deçà d'une tension d'électrode de l'ordre de —0.65 V/E.C.S. (Fig. 9). Ce comportement est vraisemblablement dû au fait que l'on se rapproche de la tension d'équilibre du système, et que la réaction cesse d'être totalement irréversible. Cette hypothèse est en accord avec les

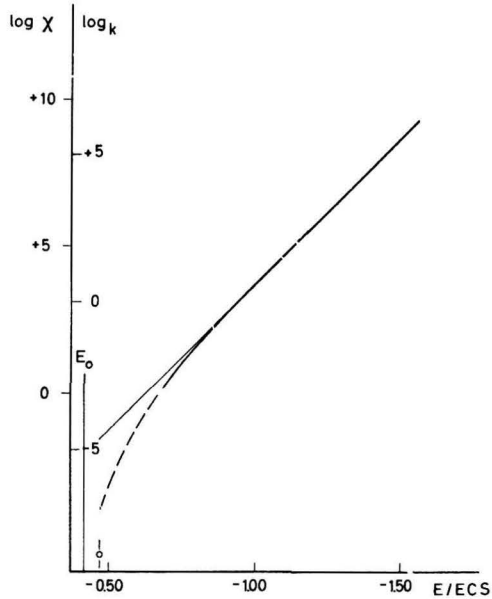

Fig. 9. Influence de la tension d'électrode sur la constante cinétique vraie de réduction de l'ion chromate (E_0 est le potentiel d'équilibre évalué à partir des données de LATIMER).

données thermodynamiques de LATIMER qui conduisent à assigner à la réaction (6) une tension d'équilibre de l'ordre de —0.42 V à pH 14 et avec le fait que l'onde d'oxydation de l'ion chromite est observable en milieu alcalin, à des tensions légèrement moins positives que celles correspondant à la courbe d'ionisation du mercure.

B. Influence de la nature et de la concentration de l'anion-support

Le choix est ici plus étendu que pour les cations, la seule limitation d'ordre pratique étant la solubilité: il y a en effet avantage à opérer à concentration élevée, de manière à ce que l'onde principale soit relativement peu rejetée vers les tensions négatives, pour lesquelles l'influence de l'anion devient négligeable. Toutes les expériences ont été effectuées en utilisant un même cation (Na^+), de manière à les rendre directement comparables.

(1) *Cas où l'influence de l'anion est négligeable.* Les ions F^-, ClO_4^-, CH_3COO^-, CO_3^{2-}, SO_4^{2-} et PO_4^{3-} ne sont pas spécifiquement adsorbés de manière décelable dans le domaine des potentiels utiles, qui s'étend au-delà d'environ —0.60 V/E.C.S. L'influence de la concentration, dans le registre compris entre 1 et 0.003 N, a été étudiée dans le cas des milieux CO_3Na_2 (*cf.* Fig. 10), SO_4Na_2 et PO_4Na_3 [dans le cas du milieu sulfate, le pH a été maintenu à 12, de manière à atténuer l'amplitude de la préonde]:

on constate que le déplacement de l'onde principale avec la force ionique est pratiquement identique à celui observé dans le milieu NaOH, ainsi que le démontre la comparaison entre les diverses valeurs de la tension de demi-onde (Tableau II). Les différences observées varient avec la charge de l'anion dans le sens prévu par la théorie de GOUY–CHAPMAN.

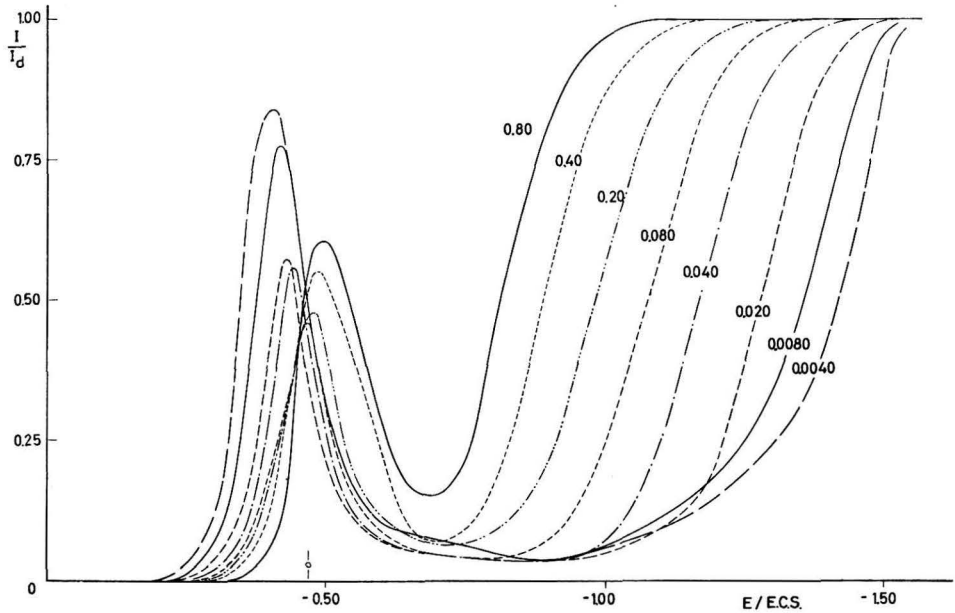

Fig. 10. Comportement polarographique de l'ion chromate $2 \cdot 10^{-4}$ *M*, en milieu CO_3Na_2 (les chiffres expriment les diverses valeurs de $[Na^+]$ en mol/l).

TABLEAU II

INFLUENCE DE LA COMPOSITION SUR LES VALEURS DE LA TENSION DE DEMI-ONDE DE L'ONDE PRINCIPALE

$[Na^+]$	*NaOH*	SO_4Na_2	PO_4Na_3	CO_3Na_2*
1	—0.78	—0.795	—0.815	—0.795
0.3	—0.90	—0.92	—0.925	—0.92
0.1	—1.015	—1.02	—1.03	—1.025
0.03	—1.185	—1.19	—1.195	—1.19
0.01	—1.32	—	—1.335	—1.32

* Valeurs interpolées et éventuellement corrigées (pour les conc. 1 et 0.3) de la présence de la préonde.

Il a par ailleurs été vérifié que les tensions de demi-onde observées dans les milieux ($NaClO_4$ + NaOH) *M* coïncident pratiquement avec la valeur trouvée en milieu NaOH *M*.

Ces divers résultats confirment le fait que l'étape cinétique déterminante est d'ordre zéro par rapport aux ions hydroxyle; ils confirment la validité du mécanisme réaction-

nel proposé, faisant intervenir la double-couche électrochimique; ils indiquent enfin que les divers anions étudiés sont pratiquement inactifs aux tensions d'électrode considérées.

(2) *Cas où l'anion est spécifiquement adsorbé.* Seuls les anions appréciablement tensioactifs sont susceptibles d'affecter la morphologie de l'onde principale. On peut prévoir que l'addition progressive de tels anions doit avoir pour conséquence d'accroître la surtension de décharge, l'effet étant le plus marqué aux tensions les moins négatives (pour lesquelles l'adsorption spécifique est la plus importante): il doit en résulter une translation des ondes vers les tensions négatives, accompagnée d'un relèvement de leur pente. Ces prévisions ont été vérifiées, pour l'ion thiocyanate, dans une série d'expériences effectuées à force ionique constante (Fig. 11).

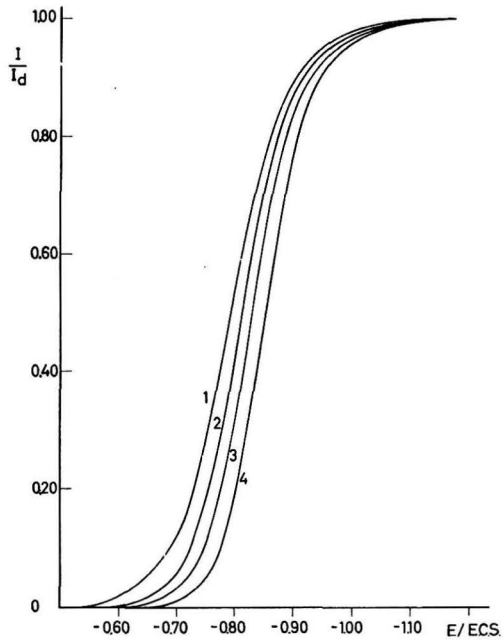

Fig. 11. Influence décélératrice de l'ion thiocyanate: $[CrO_4K_2] = 10^{-3}$ M; 1, [KOH] = 1 N, [KSCN] = 0; 2, [KOH] = 0.9 N, [KSCN] = 0.1 N; 3, [KOH] = 0.75 N, [KSCN] = 0.25 N; 4, [KOH] = 0.25 N, [KSCN] = 0.75 N.

Ainsi que l'on peut s'y attendre, l'effet retardateur dépend de la nature de l'anion tensioactif: il croît dans la série $Cl^- < Br^- < SCN^- < I^-$ (Fig. 12).

L'interprétation de l'influence de ces anions est immédiate, en termes de la théorie proposée: leur adsorption spécifique s'accompagne en effet d'une variation négative des potentiels ψ_δ, qui cessent par ailleurs de pouvoir être calculés à l'aide de la relation de GOUY–CHAPMAN, en identifiant la densité de charge de l'électrode à la charge de la partie diffuse de la double-couche. On remarquera que ces potentiels altérés peuvent, en principe, être évalués à partir de la mesure de la variation des constantes de vitesse consécutive à l'addition d'ions tensioactifs, sur la base de la relation (11). Un tel

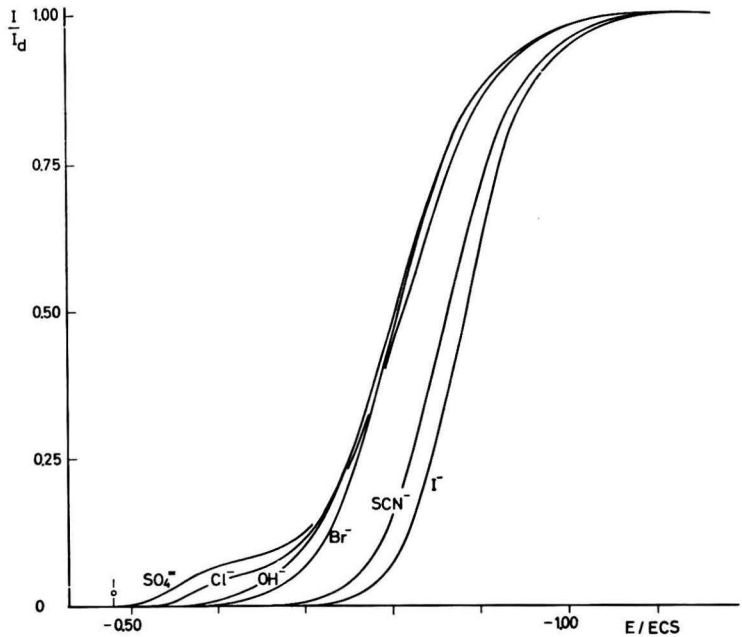

Fig. 12. Influence de l'anion-support: $[CrO_4Na_2] = 10^{-3}$ M; [KOH] = 0.25 M et [KX] = 0.75 N.

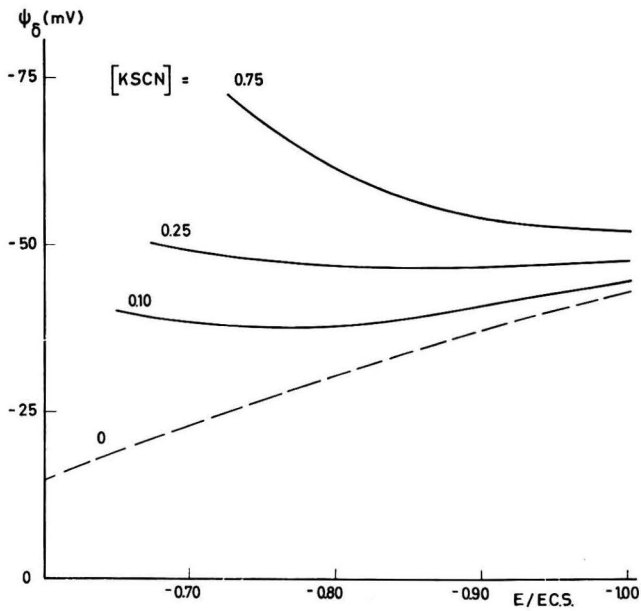

Fig. 13. Potentiels ψ_δ induits par l'adsorption spécifique de l'ion thiocyanate. Les compositions sont celles de la Fig. 11.

calcul a permis d'établir le graphique de la Fig. 13, dont il importe de souligner le caractère approché: les valeurs de ψ_δ ainsi déterminées n'ont en effet de chances d'être correctes que pour autant que, notamment, l'action de l'ion thiocyanate se limite exclusivement à modifier la densité de charge "effective" de l'électrode, sans en réduire les propriétés réactionnelles par blocage superficiel.

La Préonde

A. Considérations générales

L'expérience montre que la morphologie, la position et l'amplitude de la préonde dépendent d'un nombre élevé de facteurs, parmi lesquels les plus importants semblent être le pH, la force ionique, la concentration en chromate et la nature des ions de l'électrolyte-support.

L'ensemble des résultats indique que l'influence de la double-couche est particulièrement importante; c'est ainsi que la préonde est sensiblement affectée par la présence d'anions même relativement peu tensioactifs (tels que l'ion perchlorate, par exemple, qui n'affecte pratiquement pas l'onde principale). Par contre, l'influence du cation est relativement moins importante. Ce comportement est évidemment dû au fait que la préonde se développe à des tensions notablement moins négatives que celles qui correspondent à l'onde principale. Il résulte de cette circonstance que l'élucidation du mécanisme réactionnel sera la plus aisée dans les solutions d'électrolyte-support dont l'anion (et dans une moindre mesure, le cation) est le moins tensioactif possible. Sous ce rapport, les solutions sodiques de fluorure, sulfate, carbonate et phosphate paraissent a priori les mieux indiquées.

Dans ces milieux, l'étude du comportement mène aux constatations générales suivantes:

(1) La préonde a toujours la forme d'une courbe avec maximum ("pic"). Si elle est très proche de l'onde principale, elle peut sembler présenter un courant-limite constant, mais l'analyse de la courbe fait apparaître qu'il s'agit en réalité de la résultante de deux courants partiels, l'un croissant (onde principale) et l'autre décroissant. Cette morphologie particulière de la préonde s'observe même aux forces ioniques élevées (pour lesquelles les potentiels ψ_δ sont faibles).

(2) Toutes autres conditions égales, l'élévation de la force ionique tend généralement à déplacer négativement la position de la préonde, et à en augmenter l'amplitude, même au point de charge nulle.

(3) En milieu hydroxyde, l'amplitude croît à mesure que l'électrolyte-support est dilué, et l'on observe alors des pics assez aigus (Figs. 2 et 6). On remarquera que, dans de telles expériences, le pH et la force ionique varient simultanément, ce qui complique l'interprétation. En général, l'élévation du pH tend à abaisser la préonde et à la reculer vers des tensions plus négatives. Les milieux carbonate et phosphate constituent des cas particuliers, pour lesquels il est difficile d'établir une corrélation satisfaisante entre le pH et l'amplitude (*cf.* Figs. 10, 16 et 18). Par ailleurs, à un même pH et à force ionique égale, l'amplitude est très différente selon la composition (voir Fig. 23).

On conçoit que ces circonstances sont de nature à compliquer l'étude de l'influence du pH, qui constitue cependant le critère de diagnostic le plus important, seul susceptible de trancher entre l'hypothèse d'une décharge directe et celle d'une réaction chimique antécédente.

Choix des conditions expérimentales. Il ressort des considérations qui viennent d'être

énoncées que l'élucidation du mécanisme déterminant doit être basée sur des expériences effectuées en l'absence d'ions appréciablement tensioactifs, et à force ionique élevée, de manière à éliminer aussi efficacement que possible l'influence de la partie diffuse de la double-couche. Ce n'est qu'après s'être ainsi assuré du rôle exact du pH, qu'il sera ensuite possible d'étudier l'influence des autres facteurs déterminants.

B. Etude de l'influence du pH, à force ionique constante, et en l'absence d'ions appréciablement tensioactifs

Les milieux NaOH, NaF + NaOH, Na_2SO_4 + NaOH, Na_2CO_3, Na_3PO_4 et NH_4OH peuvent en principe être utilisés. La difficulté principale, qui explique pourquoi le comportement peut varier à même pH, selon le milieu choisi, provient de ce que la réaction éventuellement déterminante, soit $CrO_4^{2-} + H^+ \rightarrow CrO_4H^-$, peut s'effectuer par l'intermédiaire de donneurs de protons différents (H_2O, CO_3H^-, PO_4H^-, NH_4^+), avec des constantes d'équilibre et des constantes de vitesse très différentes. En fait, GREEN ET WALKLEY[7] ont émis l'hypothèse que le donneur serait HCO_3^-, dans les tampons carbonate–bicarbonate qu'ils ont utilisés. Dans les milieux carbonate, phosphate et ammoniacal, on ne peut en outre exclure la possibilité d'une réaction procédant par deux sentiers parallèles, l'un d'eux mettant en jeu les molécules d'eau. Ceci justifie l'intérêt évident qu'il y a à opérer tout d'abord dans les milieux où l'eau soit le seul donneur à considérer.

Milieux où H_2O est le seul donneur de protons présent. Cette nouvelle restriction limite les compositions aux seuls milieux NaF + NaOH et Na_2SO_4 + NaOH, la nécessité d'opérer à force ionique constante éliminant la possibilité d'utiliser des solutions ne contenant que l'hydroxyde de sodium. Dans la gamme des pH supérieurs à environ 12, la concentration en ions hydroxyle est grande, comparée à celles de ces mêmes ions produits par la réaction d'électrode. Il en va autrement dans la gamme des pH compris entre 9 et 12, les milieux tampons ne pouvant être employés.

Cette difficulté peut être tournée en opérant en milieu neutre non-tamponné, et en calculant le pH local à partir de la concentration en chromate et de l'amplitude relative I/I_d mesurée au potentiel considéré, à l'aide de la relation approchée.

$$[OH^-] = n\frac{I}{I_d}[CrO_4^{2-}]\sqrt{\frac{D_{CrO_4^{2-}}}{D_{OH^-}}} \qquad (12)$$

où n vaut 4 ou 5 selon que la réaction procède selon les mécanismes (2) ou (3).

Si l'on adopte pour les coefficients de diffusion des ions CrO_4^{2-} et OH^- les valeurs respectives $1.07 \cdot 10^{-5}$ et $5.20 \cdot 10^{-5}$ cm^2sec^{-1} (ref.[36], p. 52), on a

$$[OH^-] = \left.\begin{matrix}1.8\\2.25\end{matrix}\right\}\frac{I}{I_d}[CrO_4^{2-}] \qquad \begin{cases}n = 4\\n = 5\end{cases} \qquad (13)$$

On remarquera incidemment qu'une erreur dans le choix de la réaction stoechiometrique n'introduit qu'une erreur de pH relativement faible (un dixième d'unité environ).

Ainsi que l'indique la relation (12), il est possible de modifier le pH en opérant à concentration variable en chromate.

La Fig. 14 comprend les diverses courbes polarographiques obtenues en milieu tamponné (courbes 1 et 2) et non tamponné (courbes 3, 4 et 5). On constate que l'élé-

vation du pH déplace négativement les ondes, et en réduit l'amplitude maximum. L'aspect général semble être celui d'une préonde cinétique déformée par une dépression affectant son courant-limite. De manière à reconnaître l'influence du pH dans des conditions où le "courant-limite" soit atteint à toute composition, on a adopté la tension de —0.575 V, à laquelle l'influence de la partie diffuse de la double-couche reste relativement négligeable. Les diverses valeurs du paramètre χ, calculées pour cette tension d'électrode, ont été portées en fonction des valeurs du pH (Fig. 15).

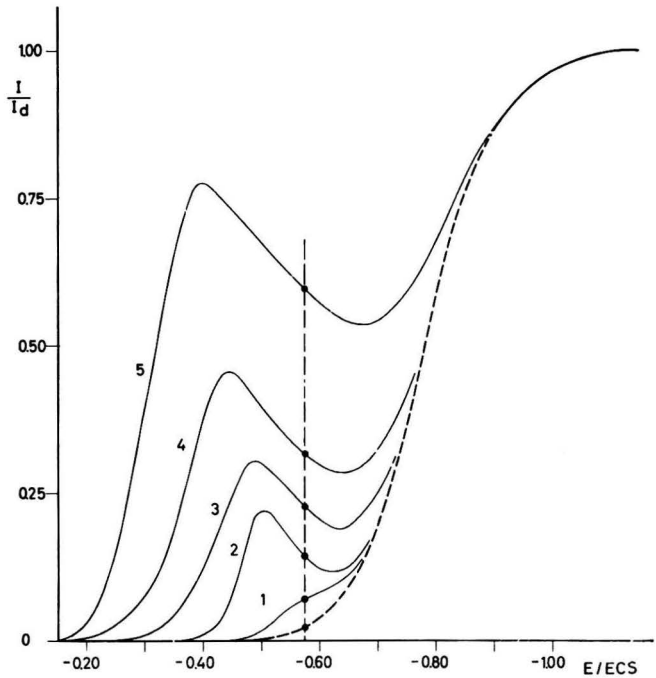

Fig. 14. Influence du pH sur la préonde (H_2O seul donneur de protons présent). Les compositions sont: 1, $[CrO_4Na_2] = 2 \cdot 10^{-4}$ M, $[NaOH] = 0.1$ N, $[NaF] = 0.8$ N; 2, $[CrO_4Na_2] = 2 \cdot 10^{-4}$ M, $[NaOH] = 0.01$ N, $[NaF] = 0.9$ N; 3, $[CrO_4Na_2] = 6.5 \cdot 10^{-3}$ M, $[NaF] = 0.9$ N; 4, $[CrO_4Na_2] = 10^{-3}$ M, $[NaF] = 0.9$ N; 5, $[CrO_4Na_2] = 10^{-4}$ M, $[NaF] = 0.9$ N.

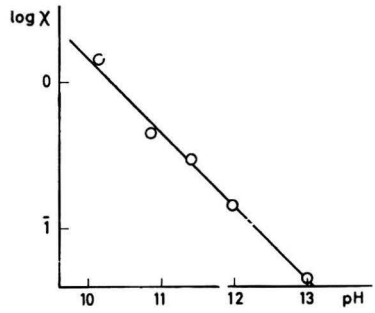

Fig. 15. Influence du pH sur l'amplitude de la préonde, mesurée à —0.575 V (en ordonnée, logarithme décimal du paramètre χ).

On constate que χ varie à peu près proportionnellement à l'inverse de la racine carrée de la concentration en ions hydroxyle, dans tout le registre du pH accessible, selon

$$\chi = \frac{B_1}{\sqrt{[OH^-]}} \quad (14) \qquad \text{avec } B_1 \approx 10^{-3.36}\ \text{mol}^{1/2}\ \text{cm}^{-3/2}. \qquad (14)$$

Cette loi est représentative d'une réaction d'électrode limitée par la vitesse de la réaction "volumique" d'ordre —1 par rapport à OH^-. Il ne peut par conséquent s'agir que de la réaction

$$CrO_4^{2-} + H_2O \rightleftharpoons CrO_4H^- + OH^- \qquad (14')$$

dont les constantes de vitesse "apparentes" valent, à —0.575 V

$$\vec{\gamma}^* \simeq 10^{2.9_5}\ \text{sec}^{-1};$$

$$\overleftarrow{\gamma}^* \simeq 10^{13.4_5}\ \text{mol}^{-1}\ \text{cm}^3\ \text{sec}^{-1}.$$

Ces valeurs sont "apparentes", car elles incluent implicitement l'influence de la partie diffuse de la double-couche, et celle de l'adsorption spécifique de l'ion chromate.

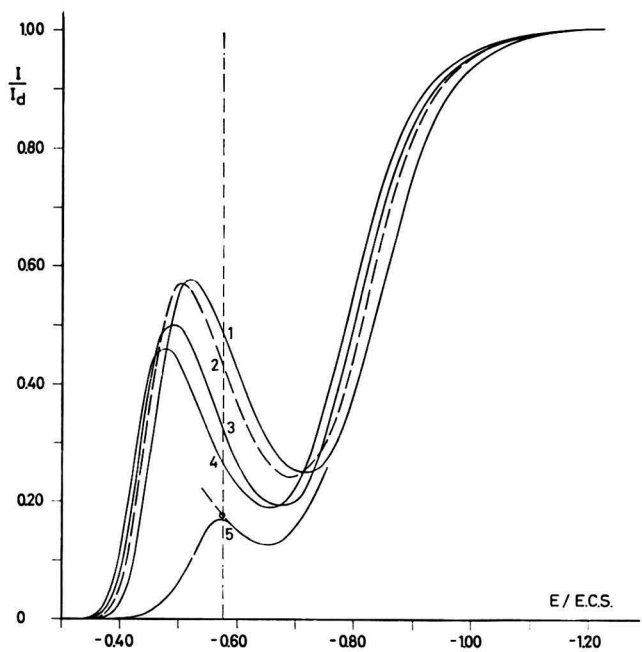

Fig. 16. Comportement de la préonde en tampon (PO_4^{3-} + PO_4H^{2-}). Les compositions sont: $[Na_2CrO_4] = 2 \cdot 10^{-4}\ M$ et 1, $[Na_3PO_4] = 0.218\ M$, $[Na_2HPO_4] = 0.173\ M$; 2, $[Na_3PO_4] = 0.109\ M$, $[Na_2HPO_4] = 0.0865\ M$, $[NaF] = 0.50\ M$; 3, $[Na_3PO_4] = 0.0654\ M$, $[Na_2HPO_4] = 0.0519\ M$, $[NaF] = 0.70\ M$; 4, $[Na_3PO_4] = 0.0218\ M$, $[Na_2HPO_4] = 0.0173\ M$, $[NaF] = 0.90\ M$; 5, $[Na_3PO_4] = M/3$.

On discutera plus loin de la possibilité d'évaluer l'ordre de grandeur des constantes cinétiques "vraies" correspondantes.

L'étalement plus marqué des ondes observées en milieu non tamponné s'explique par le fait que le pH local est d'autant plus bas que l'amplitude est petite, ce qui tend à accélérer la vitesse du processus chimique déterminant et à augmenter par conséquent la concentration locale de l'espèce $HCrO_4^-$.

En principe, le processus (14') cesse d'être déterminant au pied de l'onde: il est ainsi possible de calculer la concentration locale en $HCrO_4^-$ et d'étudier la cinétique de réduction de cet ion.

Cette méthode (qui n'est valable que pour autant que l'amplitude du courant cinétique soit suffisamment grande par rapport au courant de référence choisi au pied de l'onde, ce qui n'est pas toujours le cas ici) sera utilisée plus loin, en adoptant des conditions de milieu plus favorables.

Milieu phosphate. A même pH, la préonde est notablement plus élevée en milieu phosphate qu'en milieu non-tamponné (*cf.* Fig. 16), son amplitude décroît lorsque la capacité du tampon est abaissée, la force ionique étant maintenue constante par addition complémentaire de fluorure de sodium (*cf.* Fig. 16: courbes 1 à 4). Il est évident qu'un autre mécanisme réactionnel se superpose à la réaction mettant en jeu la molécule H_2O. De manière à élucider la nature de ce mécanisme, la méthode suivante a été utilisée (Tableau III):

TABLEAU III

PARAMÈTRES CINÉTIQUES EN MILIEU PHOSPHATE

$[HPO_4^{2-}]$ (M/l)	$[PO_4^{3-}]$ (M/l)	$\frac{I}{I_d}$ (à −0.575 V)	χ_{total}	χ_{H_2O}	χ_2
0.173	0.218	0.485	0.935	0.14	0.795
0.0865	0.109	0.435	0.78	i_d	0.64
0.0519	0.0654	0.315	0.60	i_d	0.46
0.0173	0.0218	0.270	0.40	i_d	0.26

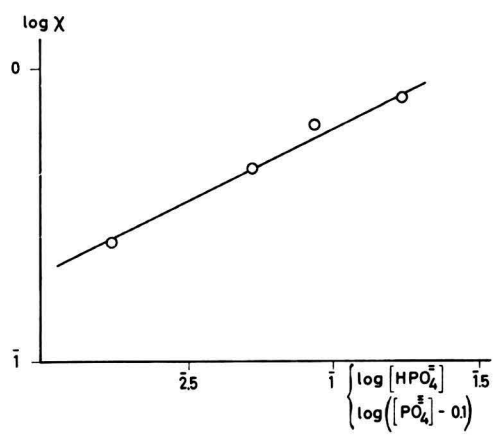

Fig. 17. Influence de la capacité du tampon (PO_4^{3-} + PO_4H^{2-}) sur l'amplitude de la préonde, mesurée à —0.575 V (en ordonnée, logarithme décimal du paramètre χ).

(1) les courants I/I_d sont mesurés à une même tension d'électrode, judicieusement choisie (soit —0.575 V) de manière à éviter l'interférence de l'onde principale, sans cependant se trouver dans la partie ascendante de la préonde;

(2) on calcule les valeurs correspondantes du paramètre χ;

(3) on défalque de ces valeurs la composante χ_{H_2O} due à la réaction parallèle utilisant H_2O comme donneur de protons (eqn. 14);

(4) les nouvelles valeurs χ_2 sont portées en fonction de la capacité du tampon, dans un diagramme bilogarithmique (Fig. 17).

On déduit de l'examen de ce diagramme que χ varie à peu près proportionnellement à la racine carrée de la capacité du tampon (droite en trait plein). Il en résulte que le comportement observé peut être décrit, a priori, par l'une quelconque des relations suivantes:

$$\chi_2 = B_2 \sqrt{[PO_4^{3-}]} \tag{15a}$$

ou

$$\chi_2 = B_2' \sqrt{[PO_4H^{2-}]} \tag{15b}$$

ou

$$\chi_2 = B_2'' \frac{[PO_4H^{2-}]}{\sqrt{[PO_4^{3-}]}} \tag{15c}$$

ou

$$\chi_2 = B_2''' \frac{[PO_4^{3-}]}{\sqrt{[PO_4H^{2-}]}} \tag{15d}$$

La relation (15c) est, dans le groupe, la seule à laquelle puisse être attachée une signification physique, à la lumière de la théorie de KOUTECKY. Elle correspond au cas où la vitesse du processus électrochimique global est limitée par celle de la réaction chimique antécédente

$$CrO_4^{2-} + HPO_4^{2-} \rightleftharpoons CrO_4H^- + PO_4^{3-} \tag{16}$$

On a effet dans ce cas:

$$\chi = [HPO_4^{2-}] \sqrt{\frac{12}{7} \frac{K \vec{r} t_g}{[PO_4^{3-}]}} \tag{17}$$

Tenant compte de ce que K, B_2'' et t_g valent respectivement $10^{-5.4}$, 70 $mol^{-1/2}\,cm^{3/2}$ et 4 sec, on calcule aisément les valeurs suivantes pour les constantes cinétiques apparentes de la réaction (16): $\vec{r}^* \simeq 10^{8.4_5}$ $mol^{-1}\,cm^3\,sec^{-1}$; $\overleftarrow{r}^* \simeq 10^{13.8_5}$ $mol^{-1}\,cm^3\,sec^{-1}$.

De manière à confirmer la validité du schéma réactionnel proposé, on a procédé à une expérience de contrôle qui a été effectuée dans le milieu PO_4Na_3 1/3 M, pour lequel le rapport des concentrations en PO_4H^{2-} et en PO_4^{2-} est modifié de manière significative.

Dans de telles conditions, on calcule que:

$$\chi_{H_2O} = 0.06 \text{ et } \chi_2 = 0.180,$$

soit un χ expérimental de l'ordre de 0.24, auquel devrait correspondre un courant d'amplitude relative 0.18. L'examen de la Fig. 16 (courbe 5) montre que l'accord

avec la courbe expérimentale est satisfaisant. Il devient excellent si l'on tient compte du fait que le courant-limite n'est pas encore tout-à-fait atteint à —0.575 V (courbe hypothétique en traits interrompus). Cette concordance confirme le schéma (16) et valide le rejet des relations empiriques (15a) (15b) et (15d) qui ne sont vérifiées que pour les quatre premières compositions.

Milieu carbonate. Comme dans les solutions de phosphate, l'amplitude de la préonde est considérablement augmentée à pH égal. Le pK du système carbonate–bicarbonate étant relativement peu élevé, l'emploi de solutions-tampons présente l'inconvénient de donner des préondes d'amplitude excessive. Cette difficulté peut être tournée en opérant en milieu carbonate de sodium à concentration variable (avec addition complémentaire d'un sel indifférent, de manière à contrôler la force ionique) (Fig. 18, courbes 1 à 4).

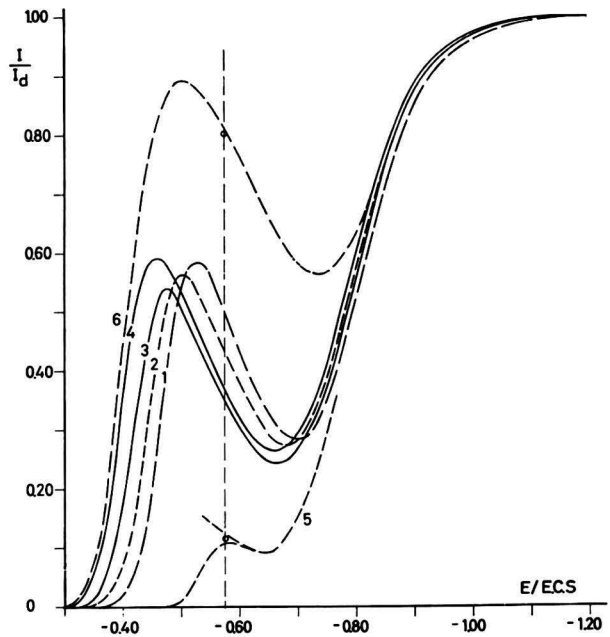

Fig. 18. Comportement de la préonde en milieu carbonate. Les compositions sont: $[Na_2CrO_4] = 2 \cdot 10^{-4}$ M et 1, $[Na_2CO_3] = 0.45$ M; 2, $[Na_2CO_3] = 0.15$ M + [NaF] = 0.6 M; 3, $[Na_2CO_3] = 0.045$ M + [NaF] = 0.81 M; 4, $[Na_2CO_3] = 0.015$ M + [NaF] = 0.87 M; 5, $[Na_2CO_3] = 0.45$ M + [NaOH] = 0.10 M; 6, $[Na_2CO_3] = 0.435$ M + $[NaHCO_3] = 0.03$ M.

TABLEAU IV

PARAMÈTRES CINÉTIQUES EN MILIEU CARBONATE

$[CO_3^{2-}]$ (M/l)	$[HCO_3^-]$ et $[OH^-]$ $(M/l \cdot 10^3)$	$\frac{I}{I_d}(-0.575\ V)$	χ_{total}	χ_{H_2O}	χ_3
0.45	9.5	0.50	0.98	0.14	0.84
0.135	5.2	0.43	0.76	0.19	0.57
0.045	3.0	0.345	0.54	0.24	0.31
0.0135	1.64	0.36	0.575	0.33	0.245

La méthode de calcul précédemment décrite a été utilisée, en tenant compte du fait que χ_{H_2O} varie d'une expérience à l'autre, puisque le pH n'est pas constant (Tableau IV).

On remarquera qu'en milieu carbonate dilué, la majeure partie du courant revient à la réaction utilisant l'eau comme donneur de protons. Il en résulte que l'évaluation

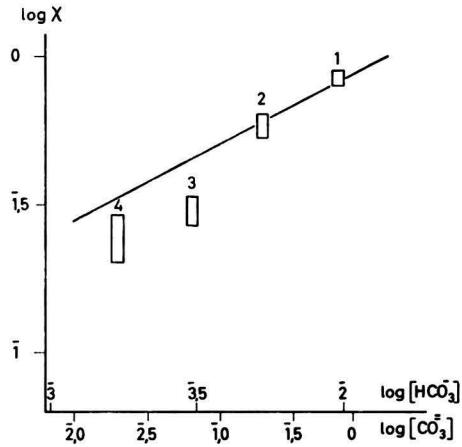

Fig. 19. Influence de la concentration en carbonate sur l'amplitude de la préonde, mesurée à —0.575 V (en ordonnée, logarithme décimal du paramètre χ). Les chiffres renvoient aux compositions correspondantes de la Fig. 18.

de la composante χ_3 spécifique au milieu carbonate devient assez imprécise, ainsi que le montre le graphique bilogarithmique de la Fig. 19 (points 3 et 4). La droite de pente 1/2, passant par les points 1 et 2, est représentative de l'équation empirique:

$$\chi = B_3 \frac{[HCO_3^-]}{\sqrt{[CO_3^{2-}]}} \tag{18}$$

(avec $B_3 \simeq 10^{3.27}$ mol$^{1/2}$ cm$^{-3/2}$) correspondant à la réaction chimique antécédente

$$CrO_4^{2-} + HCO_3^- \rightleftharpoons CrO_4H^- + CO_3^{2-} \tag{18'}$$

avec les constantes cinétiques apparentes:

$$\vec{r}^* \simeq 10^{9.50} \text{ mol}^{-1} \text{ cm}^3 \text{ sec}^{-1};$$

$$\overleftarrow{r}^* \simeq 10^{13.30} \text{ mol}^{-1} \text{ cm}^3 \text{ sec}^{-1}.$$

Ce mécanisme a été confirmé par deux expériences indépendantes, effectuées dans des milieux de composition très différentes (Fig. 18, courbes 5 et 6: les cercles représentent les valeurs théoriques de I/I_d calculées à partir des relations (14) et (18)). L'accord expérimental est satisfaisant, ce qui justifie à la fois le schéma (18') et la valeur numérique adoptée pour la constante B_3.

Milieu ammoniacal. On observe ici également une exaltation importante de la préonde, vraisemblablement liée à l'occurrence d'une réaction antécédente, utilisant NH_4^+ comme donneur de protons. Une situation analogue prévaut probablement en tampon borate*. Ces réactions n'ont pas été étudiées en détail, car elles s'effectuent à des pH défavorables, caractérisés par des préondes très élevées et la possibilité de passivation.

Morphologie et position de la préonde. Quel que soit le donneur de protons, le courant cinétique décroît sensiblement à mesure que la tension d'électrode est rendue négative. A la force ionique utilisée (soit 1), les potentiels ψ_δ ne peuvent être considérables: la partie diffuse de la double-couche n'exerce par conséquent qu'un effet de second ordre. Par contre, l'adsorption spécifique de l'ion chromate est d'autant plus considérable que la tension d'électrode est moins négative. Ce fait nous paraît expliquer pourquoi le courant cinétique s'abaisse et également pourquoi la variation relative du paramètre χ avec la tension d'électrode est pratiquement indépendante de la composition (les ions tensioactifs étant bien entendu exclus). Cette hypothèse sera corroborée plus loin, lors de l'étude de l'influence de la force ionique.

Il ressort de l'ensemble des expériences que la position du pied de la préonde dépend à la fois de l'amplitude du courant cinétique, et du pH. A même amplitude et pH variable (ces conditions sont pratiquement assurées dans les expériences 1 à 4 en milieu carbonate — voir Fig. 18), on constate que les tensions observées au pied de l'onde, dans des conditions comparables (soit par exemple pour $I = 0.05\ I_d$) varient avec le pH selon la loi empirique (valable en milieu carbonate):

$$E_{1/20} = -0.418 + 0.10\ (12\text{-pH}). \tag{19}$$

La valeur du coefficient 0.10 peut s'interpréter de manière satisfaisante, en admettant que la concentration de l'ion $HCrO_4^-$ est pratiquement à l'équilibre, et que cet ion est réduit irréversiblement, avec un coefficient de transfert de l'ordre de 0.6.

On remarquera, pour conclure l'étude de l'influence du pH, que toutes les données expérimentales obtenues à force ionique 1 sont explicables en postulant l'intervention déterminante d'une réaction chimique antécédente amenant la formation de l'ion $HCrO_4^-$, seul réductible aux tensions considérées. Dans cette série d'expériences, aucune indication ne permet de conclure que la réaction de décharge directe de l'ion chromate procède de manière significative.

C. Influence de la concentration en chromate, en l'absence d'ions tensioactifs

En *milieu tamponné*, cette influence est faible: c'est ainsi qu'à pH 12, l'amplitude relative de la préonde reste pratiquement constante, pour des concentrations en chromate comprises entre 1 et $5 \cdot 10^{-4}$ M/l. A des concentrations plus élevées, il pourrait en être autrement (comme conséquence de la courbure croissante de l'isotherme d'adsorption), mais le milieu n'est plus alors suffisamment tamponné, ce qui complique l'interprétation. L'élévation du pH n'améliore pas la situation, car la préonde est alors plus petite, et la mesure de son amplitude tend à devenir peu précise.

En *milieu neutre non tamponné*, l'influence de la concentration en chromate

* On remarquera par ailleurs que l'action accélératrice des ions Mg^{2+} s'explique aisément[10] par l'effet-tampon de la réaction $Mg^{2+} + 2\ OH^- \rightleftharpoons Mg(OH)_2$ qui maintient le pH à une valeur relativement basse.

est considérable: elle s'explique, ainsi qu'il en a été discuté précédemment, par le fait que le pH local dépend essentiellement de la valeur absolue du courant. Si l'on combine les relations (12) et (14), en admettant que χ est, en première approximation, proportionnel à $I/(I_d - I)$, on établit aisément que

$$\frac{I}{I_d - I} = \frac{Cte}{\sqrt{I}} \tag{20}$$

ou, posant $a = I_d/I$ et tenant compte de la relation d'ILKOVIC:

$$a(a - 1)^2 \div [CrO_4^{2-}] \tag{21}$$

L'amplitude est donc d'autant plus faible que la concentration en chromate est élevée. Ce fait avait déjà été signalé par KOLTHOFF ET LINGANE, et leur avait permis d'écarter l'hypothèse d'un mécanisme réactionnel amenant la formation d'une particule Cr(IV) ou Cr(V).

La relation (20) permet d'expliquer pourquoi les préondes observées en milieu non tamponné sont plus étalées qu'en solution-tampon: dans le premier cas, la concentration locale en ions hydroxyles est d'autant moins élevée que l'on se rapproche du pied de l'onde, ce qui tend à relever le courant; cet effet est partiellement compensé par l'augmentation résultante du pH.

D. Influence de la force ionique, en l'absence d'ions tensioactifs

A la tension zéro dans l'échelle rationnelle[34] de GRAHAME (soit environ $E = -0.47$ V/E.C.S.), et en l'absence d'ions tensioactifs, ψ_δ est en principe nul quelle que soit la force ionique. L'influence de la double-couche est donc nulle à cette tension particulière: c'est ce que l'on constate effectivement dans le cas de l'oxydation polarographique d'un ion tel que l'ion europium bivalent[18]. Pour l'ion chromate, par contre, l'expérience indique que l'augmentation de la force ionique entraîne un accroissement notable de l'amplitude (Fig. 20). Ce comportement peut s'expliquer si l'on tient compte du fait que l'ion chromate est adsorbé spécifiquement, ainsi que le démontre sa courbe électrocapillaire (voir Fig. 5).

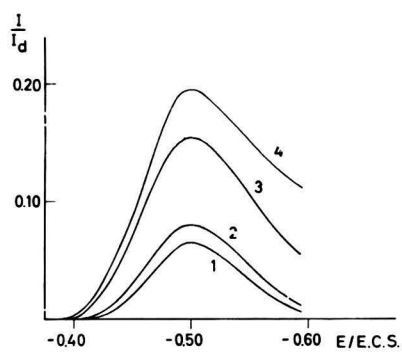

Fig. 20. Influence de la force ionique sur l'amplitude de la préonde. Les compositions sont $[Na_2CrO_4] = 2 \cdot 10^{-4}$ M; [NaOH] = 0.01 N; et 1, ———; 2, [NaF] = 0.01 M; 3, [NaF] = 0.1 M; 4, [NaF] = 0.9 M.

A force ionique faible, l'adsorption spécifique des ions chromate induit des potentiels ψ_δ relativement négatifs dans la partie diffuse de la double-couche (Fig. 21, courbe a). Si la force ionique est augmentée (courbe b), et à même charge totale de la partie diffuse, ces potentiels diminuent, ainsi que le laisse prévoir la théorie de GOUY–CHAPMAN.

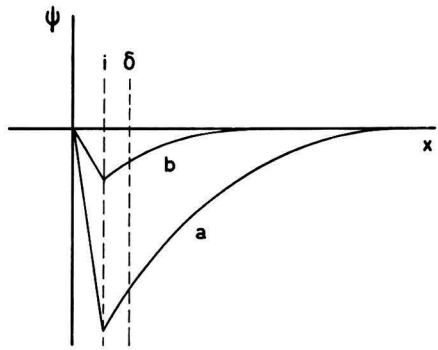

Fig. 21. Profils potentiel–distance schématiques à force ionique faible (a) et élevée (b), et à même concentration en chromate.

La quantité Γ d'ions chromate spécifiquement adsorbés

$$\Gamma = f(\varphi - \psi_i, [CrO_4^{2-}]_\delta)$$

est par ailleurs d'autant plus grande que le potentiel ψ_i au plan interne de HELMHOLTZ est négatif et que la concentration en chromate au plan δ est élevée. L'augmentation de la force ionique tend à réduire la valeur de ψ_i (qui varie parallèlement avec ψ_δ), mais accroît notablement la concentration locale $[CrO_4^{2-}]_\delta$. Il n'est pas impossible qu'au total la quantité d'ions chromate spécifiquement adsorbés se trouve augmentée, comme conséquence de l'atténuation de la charge d'espace induite par l'adsorption spécifique.

L'influence de la force ionique sur l'amplitude du courant cinétique peut dès lors se comprendre si l'on considère que le courant mesuré est la résultante de deux courants partiels, représentatifs de la réaction chimique procédant respectivement dans et en dehors de la partie compacte de la double-couche (c.-à-d. mettant en jeu les ions spécifiquement adsorbés et les autres).

Ainsi que l'indiquent les théories récentes de MATSUDA[23] et de HURWITZ[24], l'augmentation de la force ionique doit accroître la contribution "extérieure", par suite de l'atténuation de l'effet répulsif sur les partenaires réactionnels chargés négativement. La contribution "intérieure" est probablement modifiée dans le même sens. Au total, l'amplitude du courant cinétique, mesurée au point zéro de l'échelle rationnelle de GRAHAME, doit par conséquent croître avec la force ionique, en accord avec le comportement observé.

En dehors du point de charge nulle, les potentiels varient avec la force ionique, de manière complexe, en signe et en valeur. A force ionique élevée, leur influence devient négligeable: on remarque cependant que le courant-limite est loin de devenir constant,

mais qu'il continue à décroître assez rapidement dans le sens des tensions négatives. Une telle déformation est évidemment causée par la désorption progressive des ions chromate. Ceci mène à conclure qu'une fraction relativement importante du courant cinétique revient, dans de telles conditions, à la contribution "intérieure" de la réaction antécédente+. On peut en déduire que les constantes cinétiques "apparentes" $\vec{r}^*$ précédemment calculées sont probablement assez supérieures aux valeurs réelles, malgré qu'une force ionique élevée ait été utilisée: la méthode de KOUTECKY n'est en effet strictement valable qu'en l'absence totale d'effets de double-couche.

Les expériences effectuées en milieu hydroxyde, à concentration variable non compensée (Figs. 2 et 6), montrent que la préonde tend à croître avec la dilution, tout en se déplaçant vers les tensions moins négatives. Ce comportement s'explique si l'on tient compte de ce que (1) la diminution du pH a pour effet d'accroître χ et de déplacer la montée de l'onde dans le sens observé, (2) la diminution de la force ionique tend à décélérer la réaction aux charges d'électrode négatives, et à l'accélérer en deçà du point de charge nulle.

Le comportement observé à concentration variable en carbonate de sodium (Fig. 10) peut enfin s'interpréter de manière satisfaisante, si l'on considère que:

(1) la dilution décroît le pH, ce qui diminue la contribution du mécanisme mettant en jeu HCO_3^-, mais accélère la réaction utilisant H_2O comme source de protons: il en résulte que la fonction courant-limite passe par un minimum;

(2) la décroissance du pH amène par ailleurs le déplacement de la montée de l'onde vers les tensions moins négatives;

(3) la diminution de la force ionique entraîne des effets analogues à ceux exposés au cas précédent.

Ainsi que le laisse prévoir l'examen des courbes extrapolées de la Fig. 4, c'est uniquement à force ionique suffisamment faible qu'il pourrait être possible de déceler une éventuelle composante du courant dû au processus de décharge directe. En fait, cette mise en évidence ne pourrait être démonstrative qu'en opérant simultanément à force ionique faible et à pH élevé (de manière à éliminer l'interférence de la réaction chimique antécédente). Ces conditions sont évidemment totalement contradictoires, ce qui explique pourquoi l'occurrence de cette réaction ne peut être établie avec une certitude quelconque. On rappellera ici que la fonction $v = f(E)$ de la décharge directe décroît très rapidement aux tensions moins négatives qu'environ —0.65 V: ce fait suffit à expliquer pourquoi les courants extrapolés de la Fig. 4 ne sont pas observés expérimentalement.

E. Comportement en présence d'ions tensioactifs

L'introduction de quantités croissantes d'un sel dont l'anion est tensioactif a pour effet de réduire l'amplitude de la préonde, et de la déplacer vers les tensions plus négatives. La Fig. 22 montre, à titre d'exemple, l'influence des ions thiocyanate sur la préonde observée en milieu carbonate. On constate qu'à même amplitude initiale du courant (points A et B), la décélération est d'autant plus forte que la tension d'électrode est moins négative. Ce comportement reflite le fait que l'adsorption spécifique de l'ion SCN^- est d'autant moindre que la tension d'électrode est plus négative: il en résulte également que l'onde principale est relativement moins affectée par l'effet

+ Cette conclusion sera confirmée par l'étude de l'influence des anions tensioactifs.

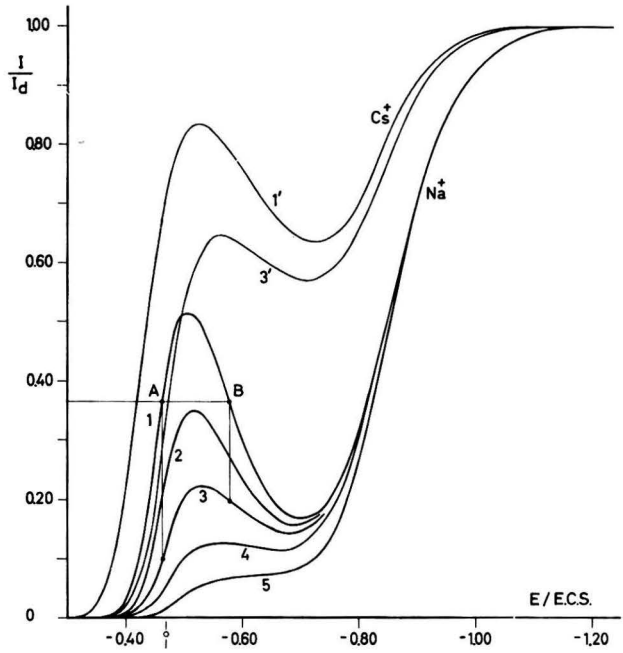

Fig. 22. Influence de l'addition de thiocyanate sur la préonde en milieu carbonate: $[CrO_4Na_2] = 2 \cdot 10^{-4}\ M$; et 1, $[Na_2CO_3] = 0.25\ M$; 2, $[Na_2CO_3] = 0.297\ M + [NaSCN] = 0.003\ M$; 3, $[Na_2CO_3] = 0.245\ M + [NaSCN] = 0.010\ M$; 4, $[Na_2CO_3] = 0.235\ M + [NaSCN] = 0.030\ M$; 5, $[Na_2CO_3] = 0.200\ M + [NaSCN] = 0.100\ M$; 1', $[Cs_2CO_3] = 0.25\ M$; 3', $[Cs_2CO_3] = 0.245\ M + [NaSCN] = 0.010\ M$.

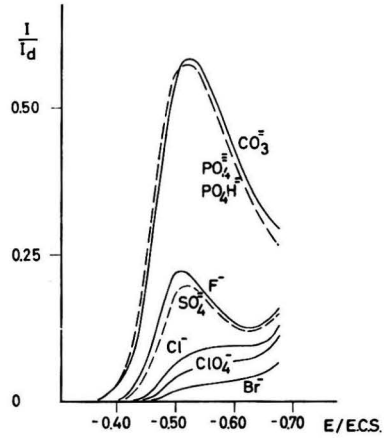

Fig. 23. Influence de la nature de l'anion-support sur la préonde, à pH 12. On a utilisé des sels sodiques avec $[Na^+] = 0.9\ M$, $[CrO_4^{2-}] = 2 \cdot 10^{-4}\ M$, et $[OH^-] = 10^{-2}\ M$. Les milieux phosphate et carbonate ont respectivement les compositions des Fig. 16, courbe 1 et Fig. 18, courbe 1.

décélérateur, ce que montre la comparaison entre les Figs. 11 et 22 ([SCN^-] = 0.1 M).

L'atténuation du pic est d'autant plus importante que l'anion est tensioactif, à même concentration. A pH 12, et en milieu molaire, les ions Cl^- et ClO_4^- agissent de manière notable, tandis que l'ion Br^- supprime presque complètement la préonde, qui disparaît totalement en milieu iodure (Fig. 23).

De manière à explorer un large domaine de tensions, il est particulièrement fructueux d'opérer dans des milieux neutres non tamponnés, pour lesquels la préonde s'étend considérablement en deçà du point de charge nulle, par suite du phénomène de l'auto-régulation du pH local, signalé précédemment.

L'examen de la Fig. 24 montre que l'ion SO_4^{2-} est pratiquement aussi inactif que l'ion F^-. Un effet plus considérable est observé avec les ions $Cl^- < ClO_4^- < NO_3^-$, dont l'action retardatrice est très voisine et croît dans l'ordre indiqué. Les ions Br^- et SCN^- sont plus actifs, quoique leur influence paraisse, à première vue, moins importante que le laisserait prévoir leur adsorbabilité.

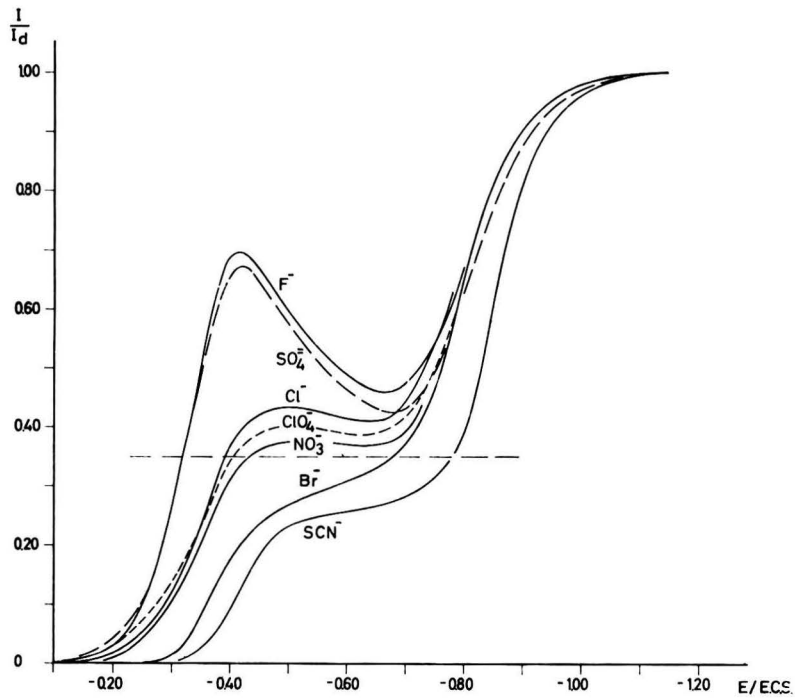

Fig. 24. Influence de la nature de l'anion-support sur la préonde, en milieu non-tamponné. [Na_2CrO_4] = $2 \cdot 10^{-4}$ M et [NaX] = 0.9 N.

Il est significatif d'observer que, dans la séquence considérée, le courant-limite de la préonde perd progressivement son aspect de "maximum" pour tendre vers une morphologie étalée (milieux Br^- et SCN^-), en passant par un état (qui serait atteint pour un ion doué de propriétés intermédiaires entre celles de NO_3^- et Br^-) où le palier serait parfaitement horizontal. On peut déduire de ce comportement que le rôle

essentiel de l'adsorption spécifique de l'anion-support est de déplacer l'ion chromate de la couche interne de HELMHOLTZ et d'annuler la contribution "intérieure" du courant cinétique, tout en exerçant une influence beaucoup plus limitée sur la contribution "extérieure" (à cet égard, il est significatif de constater que le pouvoir électrocapillaire de l'ion chromate est précisément intermédiaire entre celui des ions Cl^- et Br^-). Cette circonstance peut être mise à profit pour déterminer, par interpolation, l'amplitude du courant-limite que l'on observerait si l'ion chromate n'était pas spécifiquement adsorbé (Fig. 24: droite en traits interrompus). Quoique relativement approchée, cette méthode est la seule à permettre d'évaluer l'ordre de grandeur des constantes cinétiques vraies de l'étape chimique déterminante. Les valeurs ainsi trouvées sont certainement plus proches des paramètres réels que les constantes apparentes, calculées précédemment, sur la base des courants mesurés à —0.575 V.

Le recours à cette méthode a permis d'établir les valeurs approchées suivantes pour les diverses constantes de vitesse vraies (Tableau V).

TABLEAU V

Donneur de protons	*log K* (*mol cm*$^{-3}$)	*log* $\vec{r_0}$ (*mol*$^{-1}$ *cm*^{3} *sec*$^{-1}$)	*log* $\overleftarrow{r_0}$
H_2O	—10.5	1.8$_6$[a]	12.3$_0$
HPO_4^{2-}	— 5.4	7.4$_5$	12.4$_5$
HCO_3^-	— 3.8	7.8$_5$	11.6$_5$
NH_4^+	— 2.7	9.4$_5$	12.1$_5$
HBO_2	— 2.8	8.8$_5$	11.6$_5$

[a] sec^{-1}.

Il est significatif de constater que les valeurs des constantes cinétiques de recombinaison sont approximativement les mêmes pour les diverses réactions, et sont peu différentes du facteur de fréquence kT/h (soit environ $6 \cdot 10^{12}$ sec^{-1}). On peut en déduire que le facteur limitatif de la recombinaison n'est autre que la fréquence de collision. Une telle conclusion a déjà été tirée de l'étude de réactions acidobasiques effectuée par d'autres méthodes[35].

Il résulte de cette circonstance que l'amplitude du courant cinétique "vrai" peut être prédite, si l'on connaît la composition et le pK de la solution-tampon utilisée. La relation générale

$$\chi = [A]\sqrt{\frac{12K\vec{r_0}\,tg}{7[B]}} \tag{22}$$

où A et B sont les concentrations de l'acide et de la base du tampon, en mol cm^{-3} peut en effet se mettre sous la forme simplifiée

$$\chi = K\frac{[A]}{\sqrt{[B]}} \cdot Cte$$

(avec $Cte = \sqrt{\frac{12}{7}\frac{kT}{h}\,tg}$ soit environ $6.3 \cdot 10^6$).

Cette relation est vérifiée pour les milieux étudiés: elle l'est sans doute également pour d'autres solutions-tampons alcalines (telles que hypophosphate, éthylamine, etc.) pour

lesquelles le facteur limitatif de la recombinaison est probablement le même. La bonne concordance entre les diverses valeurs de $\overleftarrow{r_0}$ et celle du facteur de fréquence permet d'apprécier la validité de la méthode utilisée. L'accord est en général excellent, si l'on excepte le milieu carbonate, pour lequel l'évaluation précise de χ est assez difficile, du fait de la prépondérance de la réaction parallèle utilisant l'eau.

On remarquera que les calculs effectués à partir des valeurs de χ mesurées à —0.575 V en milieu non-tensioactif conduisent à des constantes apparentes de recombinaison notablement supérieures (d'environ une puissance de dix) à la limite fixée par la fréquence de collision: cette anomalie est évidemment due à l'interférence de la contribution "intérieure" au courant cinétique, provenant des ions chromate spécifiquement adsorbés.

L'influence de la nature du cation, dans le groupe des alcalins, subsiste même pour des tensions plus positives que le point de charge nulle. L'effet accélérateur (Fig. 25)

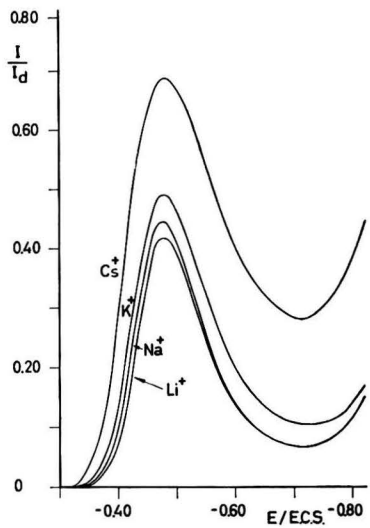

Fig. 25. Influence de la nature du cation-support sur la préonde, en milieu carbonate: $[Na_2CrO_4] = 2 \cdot 10^{-4}$ M et $[Me_2CO_3] = 0.10$ M.

croît dans la série $Li^+ < Na^+ < K^+ < Cs^+$, l'ion césium étant nettement plus actif que les trois autres cations, dont le pouvoir est peu différent (une situation identique a été observée pour l'onde principale). Ce comportement permet de conclure, en accord avec le point de vue de FRUMKIN, que l'ion césium (ainsi que les autres ions, mais dans une moindre mesure) est spécifiquement adsorbé à l'interphase. Ce fait a pour conséquence de tendre à renverser le sens de la charge spatiale associée à la partie diffuse de la double-couche, ce qui augmente la concentration locale des ions chromate et favorise par conséquent leur adsorption spécifique. L'action accélératrice de l'ion césium peut être atténuée par la présence d'anions tensioactifs. C'est ainsi que si l'on compare les milieux Na_2CO_3 et Cs_2CO_3 0.25 M (Fig. 22), on constate que l'addition de 0.01 mole de NaSCN entraîne un ralentissement $\Delta \log \chi$ à peu près semblable aux

tensions peu négatives (montée de la préonde); par contre, au delà du point de charge nulle, l'influence du thiocyanate est proportionnellement moindre en milieu césium, à mesure que la tension est rendue plus négative. Le comportement "mixte" ainsi observé dépend essentiellement de la tension d'électrode, comme on peut s'y attendre. Pour les concentrations choisies, c'est à environ —0.50 V que l'effet accélérateur de l'ion Cs^+ est exactement compensé par l'action retardatrice de l'ion SCN^-. Il en va évidemment différemment selon le rapport des concentrations: l'étude détaillée du cas "mixte" est actuellement en cours.

On remarquera, pour terminer, que l'influence spécifique du cation est relativement peu marquée dans les expériences effectuées à concentration variable en hydroxyde (voir Figs. 2 et 6). Cette circonstance s'explique par l'antagonisme entre l'accélération causée par l'augmentation du contenu cationique, et l'influence décélératrice du pH sur la vitesse de la réaction chimique antécédente.

CONCLUSIONS GÉNÉRALES

L'analyse de l'ensemble des données expérimentales a permis de mettre en évidence le rôle essentiel joué par la double-couche électrochimique, et l'influence déterminante de son profil potentiel-distance sur la morphologie des courbes polarographiques, quelle que soit la nature du mécanisme déterminant. Ce n'est qu'en tenant compte de ce fait qu'il a été possible d'élucider les mécanismes réactionnels, et d'en évaluer les paramètres cinétiques.

1. L'onde principale correspond à un processus de réduction directe par transfert électronique lent. La courbe de polarisation "vraie" (qui serait observée en l'absence d'effets de double-couche), obéit à la relation cinétique de VOLMER, avec un coefficient de transfert αn_α de l'ordre de 0.60, dans tout le registre des tensions étudiées, à la seule exception du domaine des tensions peu négatives (en deçà d'environ —0.65 V) où l'on observe une courbure décelable.

2. L'étude de l'influence de la concentration en divers donneurs de protons, dans des conditions de milieu judicieusement établies, a permis de confirmer que la préonde est effectivement déterminée par l'occurrence d'une réaction chimique antécédente du type

$$CrO_4^{2-} + Z\text{-}H \rightleftharpoons CrO_4H^- + Z^-$$

amenant de la formation de l'espèce CrO_4H^- seule réductible aux tensions considérées. Selon les milieux, Z peut être H_2O, HCO_3^-, HPO_4^{2-}, NH_4^+ et HBO_2. Ces diverses réactions peuvent procéder parallèlement, et ne diffèrent que par la valeur de leurs constantes cinétiques directes. La morphologie en "maximum" de la préonde est due à l'influence de la tension d'électrode sur l'excès superficiel en ions chromate spécifiquement adsorbés.

3. L'influence de la double-couche électrochimique peut être brièvement décrite comme suit:

(a) En l'absence d'ions appréciablement adsorbables, l'accroissement de la force ionique accélère la réaction de décharge directe (par diminution du potentiel ψ_δ) et augmente l'amplitude de la préonde (principalement par neutralisation de la charge d'espace induite par l'adsorption spécifique des ions chromate). Ainsi que le laisse prévoir la théorie de GOUY–CHAPMAN, les effets observés dépendent de la charge des ions-supports.

(b) Le remplacement du cation-support, dans l'ordre $Li^+ \rightarrow Na^+ \rightarrow K^+ \rightarrow Cs^+$, tend à accélérer les deux processus. L'effet est d'autant plus marqué que la tension d'électrode est négative; il reste décelable à des tensions plus positives que celles du point de charge nulle.

(c) Les anions tensioactifs exercent une action inverse, moins importante pour l'onde principale que pour la préonde; dans ce dernier cas, la désorption des ions chromate se traduit par l'atténuation du maximum de la préonde.

Le fait que le comportement observé en l'absence d'ions appréciablement tensioactifs soit correctement décrit par la relation de FRUMKIN, en y égalant ψ_δ^* aux valeurs correspondantes calculées à partir de la théorie de GOUY–CHAPMAN, mène à la conclusion que cette théorie est en fait suffisamment approchée, malgré son caractère approximatif, pour interpréter quantitativement la morphologie et la position des courbes de polarisation, dans un registre très étendu de forces ioniques et de tensions d'électrode. A cet égard, l'étude détaillée du comportement électrochimique de l'ion chromate semble particulièrement riche en possibilités, et le champ des diverses investigations possibles est loin d'être entièrement reconnu: nous exposerons, dans la seconde partie de cette communication, les résultats d'une étude relative au comportement observé en présence de cations tétraalkylammonium.

Au total, l'étude polarographique de l'ion chromate, illustre de manière démonstrative la stricte nécessité de tenir compte des caractéristiques structurales de l'interphase, même aux forces ioniques élevées, lorsque la réaction d'électrode procède irréversiblement et fait intervenir des particules dépolarisantes chargées.

RÉSUMÉ

La réduction polarographique de l'ion chromate peut procéder selon deux mécanismes différents (décharge directe ou étape chimique antécédente), tous deux fortement influencés par les caractéristiques électriques de l'interphase. Les paramètres cinétiques vrais de ces deux processus ont été évalués, en tenant compte de la présence de la double-couche, et de l'adsorbabilité de l'ion chromate.

SUMMARY

The polarographic reduction of the chromate ion may proceed along two different paths (direct discharge, or antecedent chemical reaction), both strongly influenced by the electrical characteristics of the interphase. The "true" rate constants of the processes have been evaluated, taking into account the presence of the double layer, and the adsorbability of the chromate ion.

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A POLAROGRAPHIC STUDY OF SOME COMPLEXES OF MOLYBDENUM

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INTRODUCTION

Catalytic waves are observed in polarographic investigations when the product of the electrode reaction undergoes further reaction with other ions or molecules in the solution. The original electroactive species or a closely related one is thereby regenerated, the net effect being the reduction or oxidation of an ion or molecule which ordinarily is not electroactive at the particular potential applied to the electrode.

A number of investigations have been concerned with the catalytic behavior of molybdenum in perchlorate solutions[1-4], and there appears to be general agreement that the catalytic reaction is one involving Mo(IV) and the perchlorate ion. Similarly, JOHNSON AND ROBINSON[5] have shown that nitrate produces a catalytic wave by reaction with Mo(III). Other workers[6] have noted that catalytic waves are drastically reduced in size by the addition of known complexing agents to the solutions containing hydrogen peroxide and Mo(VI), and the effect was attributed to complex formation.

EXPERIMENTAL

Solutions

All chemicals used in the preparation of the various solutions were reagent grade materials. The Mo(VI) solutions were prepared by dilution of a stock solution of $5.13 \cdot 10^{-2}$ *M* Na_2MoO_4. The stock solution was standardized using a Jones reductor in which the Mo(III) solution produced in the reductor was collected in a solution of ferric alum. The resulting mixture of Mo(V) and Fe(II) was titrated with a standard 0.1 *N* $KMnO_4$ solution. Details of the procedure are described by SCOTT[7].

Apparatus

The polarograph was a Sargent Model III. The galvanometer was calibrated for each shunt setting by measuring the potential drop across a precision resistor with a potentiometer. The polarographic cell was an H-cell. For the study of perchlorate solutions, one arm of the cell contained the mercury–mercurous chloride–saturated sodium chloride reference electrode which was connected to the solution compartment through an arm with a sintered glass disk. The portion of the connecting arm between the sintered glass disk and the reference electrode was filled with a 4% agar–1 *M* sodium chloride plug. The dropping mercury electrode assembly consisted of a mer-

cury reservoir attached to a capillary by a length of Tygon tubing. The capillary itself was a short section of marine barometer tubing.

Procedure

The cell was immersed in a water bath maintained at 25.0 ± 0.1°. When not in use, the solution compartment was filled with saturated sodium chloride solution. All solutions were deaerated with Linde high purity nitrogen for 15 min before the polarograms were recorded. A small amount of chloroform was placed in the bottom of the solution compartment to cover the mercury which collected and thus prevent reaction with the acid molybdate solution.

For the study of nitrate solutions, the various sodium chloride solutions mentioned above were replaced by saturated potassium chloride.

THEORETICAL

The following discussion is concerned only with the thin layer of solution which surrounds the mercury drop and in which the catalytic reaction takes place.

A number of conditions must prevail if the following analysis is to be valid. First, the catalytic current must be governed solely by the concentration of uncomplexed Mo(IV) or Mo(III) at the electrode surface. This implies that solution variables such as acidity and ionic strength must be held constant. Second, the catalytic current must be measured at a potential at which only the rate of diffusion would govern the rate of reduction of molybdenum if no catalytic reaction existed. Third, the complexing of molybdenum by any species in solution must be relatively slight in comparison with the complexing action of the substance specifically added for this purpose. Fourth, the catalytic reaction must dominate all side reactions. Fifth, the reduction at the electrode must be a stepwise addition of electrons. Sixth, the order and specific rate constants of the catalytic reactions should not be affected by the addition of complexing agents. The only way in which reducible molybdenum ions can be supplied to the electrode is by diffusion since the solution is not stirred and the effect of convection is small. If the rate of diffusion is proportional to the concentration gradient which exists in the solution between the surface of the electrode and the bulk of the solution, then the observed current will be proportional to the rate of diffusion if reduction is essentially instantaneous.

$$i = k(C - C^s) \tag{1}$$

In eqn. 1 i is the current, k is the proportionality constant, C is the molybdenum concentration in the bulk of the solution, and C^s is the molybdenum concentration at the electrode surface.

When the applied potential is high enough the molybdenum ions are reduced as rapidly as they arrive at the electrode, and C^s approaches zero.
Then,

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

A similar approach can be used if an oxidation process takes place at the electrode.

It is possible to consider an oxidation process simultaneously with a reduction process in a single system. At a sufficiently high potential we can assume that eqn. 3 represents the system.

$$\mathrm{Mo(VI)} + 2\,e \rightleftharpoons \mathrm{Mo(IV)} \tag{3}$$

For this system we can write the following equations:

$$i = k_o(C_o - C_o^s) \tag{4}$$

$$-i = k_r(C_r - C_r^s) \tag{5}$$

In eqns. 4 and 5 i is the current, k_o is the proportionality constant for the oxidized species, C_o is the concentration of the oxidized species in the bulk of the solution, C_o^s is the concentration of the oxidized species at the electrode surface, and k_r, C_r, and C_r^s are the corresponding values for the reduced species.

The concentration of Mo(IV) in the bulk of the solution is zero, and when the applied potential is great enough that Mo(VI) is reduced as rapidly as it reaches the electrode, C_o^s approaches zero.

Then we have the following:

$$i = k_o C_o \tag{6}$$

$$-i = -k_r C_r^s \tag{7}$$

$$k_o C_o = k_r C_r^s \tag{8}$$

The value of k is given by the ILKOVIČ equation as $607\ n\ m^{2/3} t^{1/6} D^{1/2}$, where n is the number of electrons involved in the reaction, m is the mass of mercury flowing in mg/sec, t is the drop time in sec, and D is the diffusion coefficient in cm^2/sec. Since n, m, and t are the same for both reduction and oxidation, if we assume that the diffusion coefficients of the oxidized and reduced species are about equal, then from eqn. 8 it follows that the instantaneous concentration of Mo(IV) at the surface of the electrode is equal to the bulk concentration of Mo(VI) in the solution.

A more rigorous theoretical treatment of the problem is given by DELAHAY[8] and leads to the same result. It should be noted that DELAHAY's derivation was made for a reversible reaction. For irreversible reactions, such as occur with most solutions of molybdenum, the rates of the forward and reverse reactions could not be overlooked if current values at potentials along the rising portion of the wave were being considered. In this case the treatment for a reversible reaction would not be applicable. However, if the current values being measured corresponded to potentials at which the rate of reaction was controlled only by the rate of diffusion of electroactive species to the electrode surface, the conditions would become the same as for a reversible reaction, that is, the rate of the forward reaction approaches infinity while the rate of the reverse reaction approaches zero.

Now if we consider the catalytic reduction of the perchlorate ion by Mo(IV) and of the nitrate ion by Mo(III), the rate of the catalytic reaction, as reflected by the increase in the current over the value observed when diffusion is the only controlling factor, is determined solely by the concentration of Mo(IV) or Mo(III) when the other solution variables are held constant. In the absence of any reaction which removes Mo(IV) or Mo(III) other than by reaction with the perchlorate ion or the nitrate ion, the dependence of the catalytic current on Mo(IV) or Mo(III) concentration can be followed by varying the concentration of Mo(VI) in the solution. Experimentally it is possible to control the Mo(IV) concentration and observe the total current which flows at a particular applied potential. If the potential selected is negative enough to insure that the reduction of Mo(VI) is diffusion controlled and an estimate can be made of the

diffusion current which would be observed if a catalytic effect did not exist, then the total current can be corrected for the residual current and the diffusion current. The remaining value is the true catalytic current.

RESULTS AND DISCUSSION

Fig. 1 shows the dependence of catalytic current on molybdenum concentration in 1 *M* $HClO_4$, and Fig. 2 gives the same information for solutions having 0.2 *M* Na_2SO_4, 0.1 *M* H_2SO_4, and 0.04 *M* KNO_3 as the supporting electrolyte.

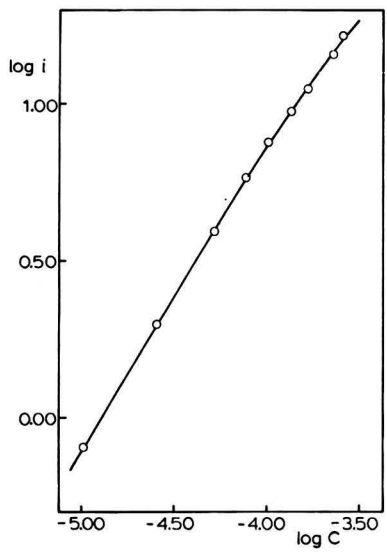

Fig. 1. The dependence of catalytic current on molybdenum concentration in perchloric acid solutions. The catalytic current, i, is measured in μA, and the molybdenum concentration, C, in moles/l.

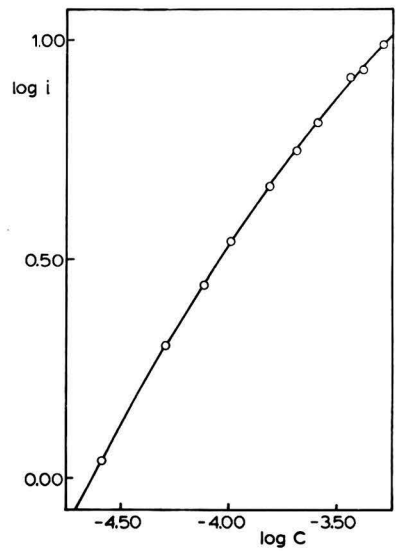

Fig. 2. The dependence of catalytic current on molybdenum concentration in nitrate solutions.

All measurements of the catalytic current in perchlorate solutions were made at —0.550 V *versus* the reference electrode while the values for the nitrate solutions were made at —0.700 V *versus* the saturated calomel electrode.

The dissociation of a complex can be presented as follows:

$$\mathrm{Mo} \cdot n\mathrm{X} \rightleftharpoons \mathrm{Mo} + n\mathrm{X} \tag{9}$$

$$K = \frac{[\mathrm{Mo}][\mathrm{X}]^n}{[\mathrm{Mo} \cdot n\mathrm{X}]} \tag{10}$$

For any particular solution the concentration of Mo(VI) and the concentration of the complexing agent are known. It has been shown that the concentration of Mo(IV) or Mo(III) at the surface of the electrode is equal to the concentration of Mo(VI) in

the bulk of the solution. If the amount of Mo(IV) or Mo(III) bound in perchlorate or nitrate complexes is small, then

$$[\mathrm{Mo}_{\mathrm{total}}] \equiv [\mathrm{Mo}] + [\mathrm{Mo} \cdot n\mathrm{X}] \tag{11}$$

The concentration of uncomplexed Mo(IV) or Mo(III) can be found from Figs. 1 and 2 through a measurement of the catalytic current. Eqn. 11 can then be used to calculate the concentration of the complex.

If eqn. 10 is put into logarithmic form and rearranged we have the following:

$$\log K = \log \frac{[\mathrm{Mo}]}{[\mathrm{Mo} \cdot n\mathrm{X}]} + n \log[\mathrm{X}] \tag{12}$$

$$\log \frac{[\mathrm{Mo} \cdot n\mathrm{X}]}{[\mathrm{Mo}]} = n\log[\mathrm{X}] - \log K \tag{13}$$

Therefore, if the left hand term in eqn. 13 is plotted *versus* the logarithm of the complexing agent concentration, a straight line should result which has a slope equal to the number of ligands per complex ion and which intercepts the ordinate at a point corresponding to the pK of the complex. If other complexes are present in appreciable concentrations, the plot will have a noticeable curvature.

Fig. 3 summarizes the experimental data obtained using 1 M $HClO_4$ as the base electrolyte, and similarly, Fig. 4 shows the results of experiments with 0.2 M Na_2SO_4–

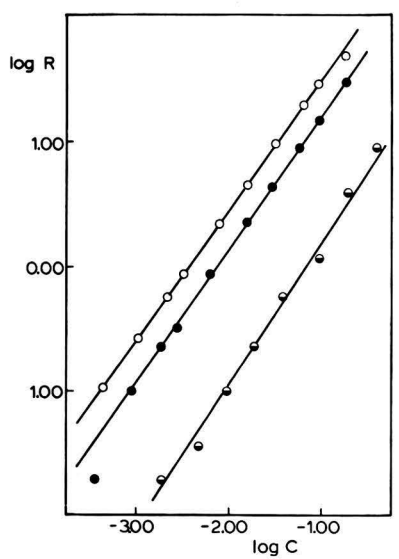

Fig. 3. The complexing effect of citric, tartaric and phosphoric acids on molybdenum in perchloric acid solutions: ○, citric acid; ●, tartaric acid; ◒, phosphoric acid.

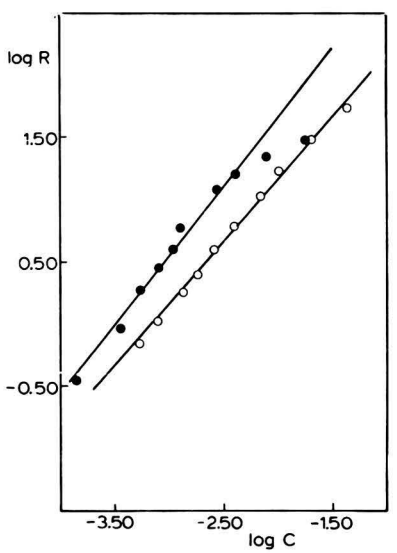

Fig. 4. The complexing effect of citric and tartaric acids on molybdenum in nitrate solutions: ●, citric acid; ○, tartaric acid.

0.1 M H_2SO_4–0.04 M KNO_3 as the base electrolyte*. A tabulation of values of n and K, as evaluated graphically, is given in Table I.

TABLE I

THE EVALUATION OF n AND K

Complexing agent	*Perchlorate solutions*		*Nitrate solutions*	
	n	K	n	K
Citric acid	1.04	$3.8 \cdot 10^{-3}$	1.13	$3.4 \cdot 10^{-4}$
Tartaric acid	1.06	$8.7 \cdot 10^{-3}$	0.99	$6.8 \cdot 10^{-4}$
Phosphoric acid	1.12	$6.9 \cdot 10^{-2}$		

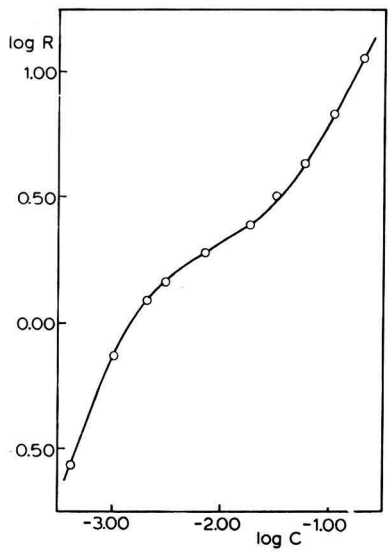

Fig. 5. The complexing effect of oxalic acid on molybdenum in perchloric acid solutions.

The pronounced bend in the plot of log K *versus* the citric acid concentration in Fig. 4 is probably due to the catalytic reduction of citric acid.

Emphasis should be placed on the fact that the values of K are formal instability constants. Further, with the solutions containing sulfate, the values of K are relative to the instability constant of any sulfate complex of Mo(III) which might exist.

Oxalic acid is known to form rather stable complexes with the various oxidation states of molybdenum[9,10], and on this basis it was selected for use in this investigation. Fig. 5 is the plot based on eqn. 13. The unusual shape of the curve is immediately apparent, and the phenomenon responsible for it was found to be characteristic of this series of solutions since the curve is reproducible.

The polymerization of molybdenum species in solution is known to be a property which is dependent upon both acidity and the presence of other ions or molecules in the solution. Under the conditions of this experiment the acidity was held constant

* R is the ratio of the concentration of complexed molybdenum to the concentration of uncomplexed molybdenum. C is the concentration of the acid, in moles/l.

by making the solutions one molar in perchloric acid. This acidity level is not affected to any appreciable extent by the addition of oxalic acid. Breaking down of higher polymeric species by a complexing action is also unlikely because complexing was noted already at very low concentrations of oxalic acid. It appears that the preliminary and final portions of the curve have roughly the same slope. This indicates that no drastic change takes place in the complex species over this particular concentration range of oxalic acid.

Another possibility to be considered in connection with the peculiar shape of the curve in Fig. 5 is the formation of more than one complex. As the simplest case let us assume that two complexes are formed. The equilibrium expressions for these two complexes are as follows:

$$\mathrm{Mo(IV)} \cdot \mathrm{H_2C_2O_4} \rightleftharpoons \mathrm{Mo(IV)} + \mathrm{H_2C_2O_4} \tag{14}$$

$$K_1 = \frac{[\mathrm{Mo(IV)}][\mathrm{H_2C_2O_4}]}{[\mathrm{Mo(IV)} \cdot \mathrm{H_2C_2O_4}]} \tag{15}$$

$$\mathrm{Mo(IV)} \cdot 2\mathrm{H_2C_2O_4} \rightleftharpoons \mathrm{Mo(IV)} + 2\mathrm{H_2C_2O_4} \tag{16}$$

$$K_2 = \frac{[\mathrm{Mo(IV)}][\mathrm{H_2C_2O_4}]^2}{[\mathrm{Mo(IV)} \cdot 2\mathrm{H_2C_2O_4}]} \tag{17}$$

If C_m is the total concentration of molybdenum, then it is possible to use eqns. 15 and 17 to express the dependence of the ratio of complexed molybdenum to uncomplexed molybdenum on the oxalic acid concentration.

$$[\mathrm{Mo(IV)}] = C_m - [\mathrm{Mo(IV)} \cdot \mathrm{H_2C_2O_4}] - [\mathrm{Mo(IV)} \cdot 2\mathrm{H_2C_2O_4}] \tag{18}$$

$$\frac{C_m - [\mathrm{Mo(IV)}]}{[\mathrm{Mo(IV)}]} = \frac{[\mathrm{Mo(IV)} \cdot \mathrm{H_2C_2O_4}] + [\mathrm{Mo(IV)} \cdot 2\mathrm{H_2C_2O_4}]}{[\mathrm{Mo(IV)}]} \tag{19}$$

$$\log\left(\frac{C_m - [\mathrm{Mo(IV)}]}{[\mathrm{Mo(IV)}]}\right) = \log\left(\frac{[\mathrm{H_2C_2O_4}]}{K_1} + \frac{[\mathrm{H_2C_2O_4}]^2}{K_2}\right) \tag{20}$$

Eqn. 20 shows that if two complexes are present together in solution, the plotting of the quantity on the left hand side of the equation *versus* the logarithm of the oxalic acid concentration would not result in a straight line but a curve which bends upward from the abscissa. If more than two complexes were formed, the number of terms on the right hand side of eqn. 20 would be increased at the rate of one for each additional complex.

However Fig. 5 does not exhibit such a shape but actually bends in the opposite direction in the range of 10^{-3}–10^{-2} molar oxalic acid. Therefore it does not seem possible that a mixture of complexes is responsible for the phenomenon.

The most plausible explanation for the shape of Fig. 5 rests in the fact that oxalic acid is probably catalytically reduced by Mo(IV). The reduction of oxalic acid at the dropping mercury electrode has been reported recently[11,12], and a catalytic reduction of oxalate in uranyl solutions was discovered by GRABOWSKI AND GRABOWSKA[13]. These workers postulated that the reduction of oxalate proceeded by means of formation of a $U^{IV}(C_2O_4)_2$ complex. Since the solution chemistry of uranium and molybdenum

is analogous in many respects, it seems reasonable to expect that the electrochemical behavior should also be similar.

Further evidence for the catalytic reduction of oxalic acid was obtained by observing the polarographic behavior of Mo(VI) in a series of solutions containing $8.16 \cdot 10^{-4}$ *M* Na_2MoO_4 in 0.1 *M* HCl with varying amounts of $Na_2C_2O_4$. The lower curve in Fig. 6 resulted from a solution containing no $Na_2C_2O_4$, and the upper curve from a solution which was $1.84 \cdot 10^{-3}$ *M* with respect to $Na_2C_2O_4$. Current values were measured at —0.150 V, —0.450 V, and —0.900 V *versus* the saturated calomel electrode, and Fig. 7 shows the remarkable increase in current which occurred at —0.450 V in comparison with the increase at —0.150 V or —0.900 V.

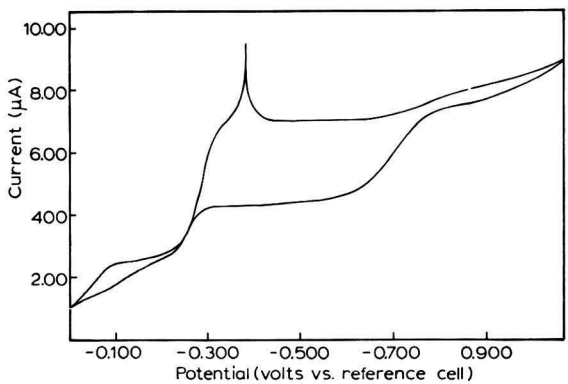

Fig. 6. The polarographic reduction of Mo(VI) in solutions of 0.1 *M* HCl and $Na_2C_2O_4$.

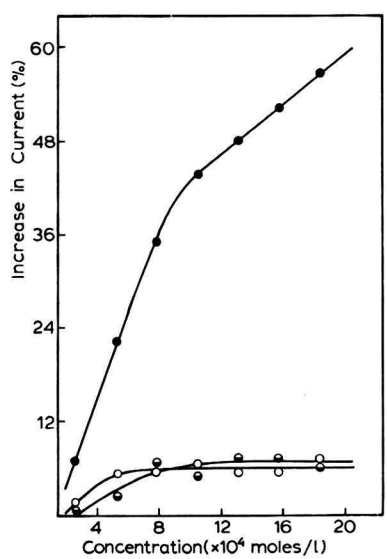

Fig. 7. The dependence of wave height on oxalate concentration: ◒, —0.150 V; ●, —0.450 V; ○, —0.900 V.

The addition of sodium oxalate to these solutions could be expected to bring about a conversion of the molybdenum species from chloride complexes to oxalate complexes with a corresponding change in the diffusion coefficient. Referring to Fig. 7, we see that the currents measured at —0.150 V and —0.900 V increased by almost an identical amount in this particular series of solutions. If it is assumed that these currents are controlled by diffusion of the complexes and the ILKOVIČ equation is applicable, then the diffusion coefficient of the Mo(VI) species will control the rate of transport of reducible ions to the electrode. The effect of the addition of oxalic acid on solution parameters such as ionic strength and viscosity and on the diffusion coefficient of the Mo(VI) species in theory will affect the heights of all waves equally. The reason for this is the fact that the rate of diffusion of the Mo(IV) species determines the quantity of material reduced at the electrode. Such should be the case for the two waves under consideration here. Furthermore since reduction at —0.900 V must result in the formation of Mo(III), the wave measured at —0.150 V is due to reduction of Mo(VI) to Mo(V) as the wave height is very close to one-third of the total wave height (within 2%).

The enhanced height of the wave measured at —0.450 V must be due to the catalytic reduction of oxalate ion or oxalic acid by Mo(IV). When the potential of the electrode is such that Mo(VI) is reduced to Mo(V) or Mo(III), no unusual behavior is observed. Only at intermediate potentials where Mo(IV) may be formed is the abnormal increase in current apparent.

Returning to consideration of Fig. 5, the peculiar shape of the wave can now be attributed to the catalytic reduction of oxalic acid by Mo(IV). This reaction probably requires the formation of a complex as a preliminary step. Therefore until complex formation is virtually complete, the instability constant of the complex will help to determine the rate of reaction along with the specific rate constant. The first two points in Fig. 5 represent conditions where the catalytic current due to the reduction of perchlorate dominates that due to the reduction of oxalic acid. The following five points are found in the area of greatest curvature and show that in this region the catalytic current due to oxalic acid reduction is an appreciable fraction of the total catalytic current. The oxalic acid catalytic current continues to increase as the perchlorate catalytic current decreases because of the complexing of Mo(IV) by oxalic acid. The net effect of this situation is an apparent loss of complexing ability on the part of oxalic acid. In reality the instability constant of the complex probably does not vary, but rather only the rates of the two catalytic reactions change. The remaining three points on the curve show the conditions where complex formation is almost complete, and as the catalytic current due to oxalic acid reduction assumes a more or less constant value, the greatest rate of change in the total catalytic current is once again due to the changing rate of the perchlorate reduction. Thus the Mo(IV)–oxalic acid complex appears to be less stable than it actually is because of the constant rate of the oxalic acid reduction. The increments of current when converted to molybdenum concentrations by means of Fig. 1 are uniformly high.

APPLICATION

The quantitative polarographic determination of molybdenum in perchloric or nitric acid solutions depends on an accurate measurement of the total current which includes both diffusion and catalytic components. Under some conditions the total current

is directly proportional to the molybdenum concentration, and under other conditions a calibration curve is necessary. Stringent control of acidity, perchlorate or nitrate concentration, and even to a certain extent, the concentration of other ions is necessary to insure a successful quantitative procedure.

An obvious extension of the material presented up to this point is the use of a complexing agent to completely suppress the catalytic wave, leaving only the normal diffusion current to be measured. Complete suppression of the catalytic wave lowers the sensitivity of the method, but on the other hand the concentrations of perchlorate or nitrate and the non-reducible ions in the solution do not have to be closely controlled.

TABLE II

THE EVALUATION OF DIFFUSION CURRENT CONSTANTS IN PERCHLORATE SOLUTIONS

The supporting electrolyte was 0.1 *M* $HClO_4$ and 0.1 *M* citric acid. The first wave was measured at —0.250 V *versus* the reference electrode, and at this potential the drop time was 3.84 sec and the mass of mercury was 2.375 mg/sec. The second wave and the total wave were measured at —0.800 V *versus* the reference electrode, and at this potential the drop time was 3.84 sec and the mass of mercury was 2.369 mg/sec. The units of I_d are $\mu A\ mg^{-2/3}\ sec^{1/2}\ mmoles^{-1}\ l$.

Mo(VI) concentration (moles/l)		*I_d of first wave*		*I_d of second wave*		*I_d of total wave*
$2.57 \cdot 10^{-5}$		1.35		3.05		4.39
$5.13 \cdot 10^{-5}$		1.39		3.11		4.50
$7.70 \cdot 10^{-5}$		1.41		3.03		4.45
$1.026 \cdot 10^{-4}$		1.47		3.06		4.53
$2.57 \cdot 10^{-4}$		1.44		2.96		4.41
$5.13 \cdot 10^{-4}$		1.45		2.97		4.42
$7.70 \cdot 10^{-4}$		1.45		2.96		4.41
$1.026 \cdot 10^{-3}$		1.45		2.95		4.40
$2.57 \cdot 10^{-3}$		1.44		2.87		4.31
	Average	1.45 ± 0.03	*Average*	3.00 ± 0.06	*Average*	4.42 ± 0.04

TABLE III

THE EVALUATION OF DIFFUSION CURRENT CONSTANTS IN NITRATE SOLUTIONS

The supporting electrolyte was 0.1 *M* HNO_3 and 0.5 *M* citric acid. The first wave was measured at —0.250 V *versus* the saturated calomel electrode, and at this potential the drop time was 3.41 sec and the mass of mercury was 2.573 mg/sec. The second wave and the total wave were measured at —0.700 V *versus* the saturated calomel electrode, and at this potential the drop time was 3.44 sec and the mass of mercury was 2.577 mg/sec. The units of I_d are $\mu A\ mg^{-2/3}\ sec^{1/2}\ mmoles^{-1}\ l$.

Mo(VI) concentration (moles/l)		*I_d of first wave*		*I_d of second wave*		*I_d of total wave*
$2.57 \cdot 10^{-5}$		1.45		2.87		4.31
$5.13 \cdot 10^{-5}$		1.43		2.83		4.25
$7.70 \cdot 10^{-5}$		1.36		2.85		4.21
$1.026 \cdot 10^{-4}$		1.32		2.82		4.15
$2.57 \cdot 10^{-4}$		1.29		2.81		4.10
$5.13 \cdot 10^{-4}$		1.30		2.80		4.09
$7.70 \cdot 10^{-4}$		1.29		2.79		4.07
$1.026 \cdot 10^{-3}$		1.27		2.79		4.06
$2.57 \cdot 10^{-3}$		1.27		2.78		4.04
	Average	1.33 ± 0.05	*Average*	2.82 ± 0.02	*Average*	4.14 ± 0.08

Since citric acid forms the most stable complex in both perchlorate and nitrate solutions, the experimental data cited earlier was used to estimate the amount of citric acid necessary to completely suppress the catalytic waves in 0.1 *M* $HClO_4$ and 0.1 *M* HNO_3.

The polarographic waves were very well-defined, and the diffusion current was easily measured. Tables II and III are tabulations of the diffusion current constants, and it can be seen that the quantitative determination of molybdenum is feasible in these solutions.

SUMMARY

The catalytic current due to the reduction of perchlorate by Mo(IV) or of nitrate by Mo(III) can be decreased by complexing these molybdenum species. When only one complex forms, the instability constant and the ratio of complexing agent to molybdenum can be evaluated. When the catalytic waves are completely suppressed, only the normal polarographic waves appear. The latter can be used to determine molybdenum quantitatively without the necessity of a calibration curve.

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ANWENDUNGEN DER AMINOVERBINDUNGEN IN DER POLAROGRAPHIE ANORGANISCHER STOFFE

XII. DIE BESTIMMUNG VON KADMIUM, BLEI UND THALLIUM IN INDIUM

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Das vor kurzer Zeit noch offene und oft diskutierte Problem der gleichzeitigen polarographischen Bestimmung von Indium und Kadmium wird bisher nur durch zwei Methoden gelöst. Bei der ersten wird als tragender und komplexbildender Elektrolyt eine alkalische Aethylendiamin-Lösung verwendet, in der sogar die gleichzeitige direkte Bestimmung von Thallium, Kupfer, Kadmium und Blei in Indium möglich ist[1,2]; bei der zweiten Methode wird als komplexbildender Elektrolyt eine Jodidlösung verwendet, in der einmal die gleichzeitige Bestimmung beider Elemente möglich ist, einmal die Bestimmung von Indium in Kadmium[3]. In dieser Mitteilung ist die Möglichkeit der direkten polarographischen Bestimmung von Thallium und Kadmium neben Indium angedeutet, gegebenenfalls die Bestimmung von Thallium und Blei neben Indium. Als Komplexbildner wird eine alkalische Lösung von bis-(2-hydroxybutyl)-2-hydroxyethylamin verwendet.

EXPERIMENTELLER TEIL UND RESULTATE

Reagenzien und Apparatur

Eine 0.01 *M* Lösung von Indium-(III)-Sulphat wurde durch dreimaliges Abdampfen (fast zum Trockenen) von 0.2869 g fein gepulverten metalischen Indium (99.95%) mit 20 ml 1 *M*-H_2SO_4 vorbereitet. Der Rückstand wurde in Wasser gelöst, mit einigen Tropfen Perchlorsäure angesäuert, in einen 250-ml Masskolben gebracht und mit redestilliertem Wasser aufgefüllt. Die übrigen verwendeten Lösungen wurden durch Lösen der entsprechenden Menge des Salzes von höchster erreichbarer Reinheit in destilliertem Wasser bereitet. Die Lösung des komplexbildenden Elektrolyten und die Apparatur sind dieselben wie in der vorgehenden Mitteilung[4].

Wie bereits gesagt wurde, bildet Indium im Medium von bis(2-hydroxypropyl)-2-hydroxyethylamin und bis(2-hydroxybutyl)-2-hydroxyethylamin (weiter nur A_2 und A_3) einen weissen Niederschlag, der durch Zugabe von alkalischem Hydroxyd gelöst wird[4]. Die Reduktion der komplex-gebundenen In-(III)-Ionen im Medium von A_2 oder A_3 in Gegenwart von alkalischem Hydroxyd an der Quecksilbertropfelektrode macht sich durch eine gut entwickelte polarographische Welle bemerkbar. Das an der Kurve entstehende rundliche Maximum kann nicht unterdrückt werden.

Durch herabsetzen der Aminoalkoholkonzentration wird die Wellenhöhe herabgesetzt (Herabsetzung der Viskosität der Lösung), das Halbwellenpotential wird zu mehr positiven Werten verschoben. Das erscheiben des Halbwellenpotenzials in Abhängigkeit von der Aminoalkoholkonzentration ist für 0.5 M-NaOH in Tabelle I angeführt.

TABELLE I

HALBWELLENPOTENZIALE VON INDIUM IN ABHÄNGIGKEIT VON DER KONZENTRATION VON AMINOALKOHOL IN DER LÖSUNG (0.1 M-NaOH, A_3)

$A_3(M)$	$E_{1/2}(V)$
0.8	—1.59
0.5	—1.57
0.1	—1.53
0.05	—1.49
0.01	—1.43
0.005	—1.38[a]
0.001	—1.27[a]
0.0005	—1.15[a]

[a] Nach einer Weile wird ein Niederschlag gebildet.

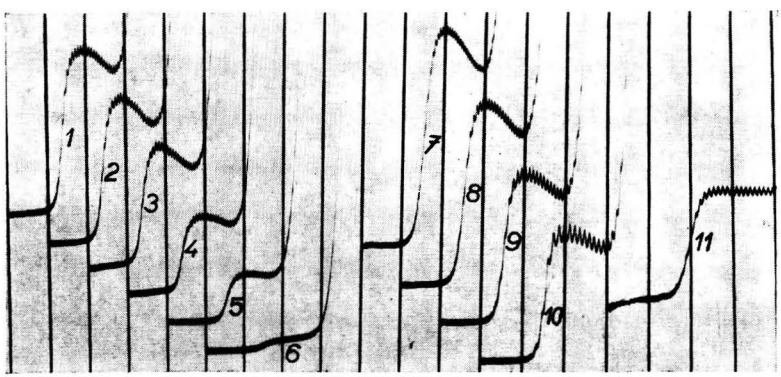

Fig. 1. Abhängigkeit der Höhe der Welle von Indium von seiner Konzentration in der Lösung und von der Reservoirhöhe: 0.5 M-A_3, 0.1 M-NaOH; (1), (7), (8), (9), (10), 10^{-3} M-In^{3+}; (2), $8 \cdot 10^{-4}$ M-In^{3+}; (3), $6 \cdot 10^{-4}$ M-In^{3+}; (4), $4 \cdot 10^{-4}$ M-In^{3+}; (5), $2 \cdot 10^{-4}$ M-In^{3+}; (6), reines Elektrolyt; (11), $5 \cdot 10^{-4}$ M-Tl^{+} in 0.1 M-NH_3 und 0.1 M-NH_4Cl. Kurve (11) ab 0 V, die anderen ab —1.2 V. Kurven (1) bis (6), (8) und (11), h = 64 cm; (7), h = 81 cm; (9), h = 49 cm; 10), h = 36 cm; S.C.E.; kathodische Polarisation; 200 mV/Absz.; Empf. 1/30.

Damit das Indium nicht die Bestimmung der anderen Elemente störe, d.h. damit die Reduktion der In-(III)-Ionen bei genügend negativen Potenzialen verläuft, muss mit genügend konzentrierten Aminoalkohol-Lösungen gearbeitet werden. Im weiteren wurde mit 0.5 M-A_3 oder 0.5 M-A_2 gearbeitet, andere Aminoalkoholkonzentrationen wurden nicht untersucht.

Die Halbwellenpotenziale, die der Reduktion von Indium entsprechen sind von der

Konzentration des alkalischen Hydroxyds sehr wenig anhängig. Bei längerem Stehen der Lösungen (über drei Stunden) wird die Indium-Welle um etwa 30 bis 50 mV in Richtung der mehr negativen Werte verschoben, Ihre Höhe bleibt unverändert.

Die Höhe der Welle ist eine lineare Funktion der Konzentration von Indium in der polarographierten Lösung, auch die Abhängigkeit der Wellenhöhe von der Quadratwurzel der Reservoirhöhe ist linear (Fig. 1).

Das Halbwellenpotenzial, das der Reduktion von komplex gebundenen Kadmium Ionen in 0.5 *M*-Aminoalkohol entspricht ist stark von der Menge des alkalischen Hydroxyds in der Lösung abhängig. Aus Tabelle II geht hervor, dass die grösste

TABELLE II

HALBWELLENPOTENZIALE VON KADMIUM UND BLEI IN 0.5 *M*-A_3—ABHÄNGIGKEIT VON DER KONZENTRATION AN ALKALISCHEM HYDROXYD (NaOH)

NaOH(M)	$E_{1/2}(V)$	
	Cd^{2+}	Pb^{2+}
1	—1.26	—1.29
0.5	—1.19	—1.23
0.1	—1.07	—1.16
0.05	—1.02	—1.11
0.01	—0.93	—0.94
0	—0.78	—0.85

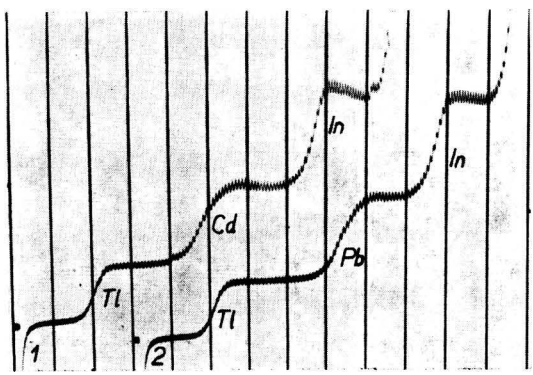

Fig. 2. Polarographisches Spektrum von Tl^+, Cd^{2+}, Pb^{2+} und In^{3+}: 0.5 *M*-A_3, 0.1 *M*-NaOH; Kurve (1), $5 \cdot 10^{-4}$ *M*-Tl^+, $5 \cdot 10^{-4}$ *M*-Cd^{2+}, $5 \cdot 10^{-4}$ *M*-In^{3+}; Kurve (2), $5 \cdot 10^{-4}$ *M*-Tl^+, $5 \cdot 10^{-4}$ *M*-Pb^{2+}, $5 \cdot 10^{-4}$ *M*-In^{3+}; S.C.E.; O V; kathod. Polarisation; $h = 64$ cm; 200 mV/Absz.; Empf. 1/30.

Differenz der Halbwellenpotenziale von Kadmium und Indium in Lösungen auftritt, in denen die Hydroxydkonzentration kleinstmöglich ist. Eine niedrige Konzentration an alkalischem Hydroxyd hat aber den Nachteil, dass das Indium mit der Zeit aus der Lösung ausgeschieden wird, und zweitens dass dann die Kadmiumwellen noch mehr langgezogen erscheinen. Die geeignetste Hydroxydkonzentration für 0.5 *M*-A_3 ist also 0.1 *M*. Unter diesen Bedingungen hat die Welle Diffusionscharakter.

Das Blei bildet im Medium von 0.5 *M*-Aminoalkohol eine gut entwickelte Welle,

deren Halbwellenpotenzial (ähnlich wie bei dem Kadmium) durch Zugabe von Hydroxyd zu mehr negativen Werten verschoben wird. Aus Tabelle II ist zu sehen, dass es in dem verwendeten Elektrolyt nicht möglich ist die Wellen von Blei und Kadmium voneinander zu trennen.

Der Diffusionscharakter der Welle in dem untersuchten Medium (0.5 *M*-A_3, 0.1 *M*-NaOH) ist durch die direkte Proportionalität der Wellenhöhe einmal der Konzentration der Blei-Ionen in der Lösung, einmal der Quadratwurzel der Reservoirhöhe gegeben.

Das Halbwellenpotenzial (—0.47 V) noch auch die Höhe der Difussionswelle von Thallium werden fast gar nicht von der Konzentration des alkalischen Hydroxyds in der Lösung beeinflusst.

Aus den Differenzen der Halbwellenpotenziale der untersuchten Elemente ist es klar, dass im Medium von 0.5 *M*-A_3 und 0.1 *M*-NaOH die Wellen von Thallium, Kadmium und Indium, gegebenfalls von Thallium, Blei und Indium getrennt werden können, und das die besagten Elemente bestimmt werden können. Bei der Bestimmung von Kadmium, Blei und Thallium in Indium stört Indium in dem Falle, wenn es in hundertfachem (molarem) Überschuss gegenüber den zu bestimmenden Elementen anwesend ist. Das polarographische Spektrum ist in Fig. 2 angeführt.

ZUSAMMENFASSUNG

Die Möglichkeit der polarographischen Bestimmung von Thallium und Kadmium neben Indium eventuell von Thallium und Blei neben Indium, im Medium von 0.5 *M* bis-(2-hydroxybutyl)-2-hydroxy-äthylamin mit 0.1 *M* NaOH als Elektrolyt ist beschrieben.

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POTENTIOMETRIC STUDY OF THE OXIDATION OF TRIVALENT MOLYBDENUM BY LEAD TETRAACETATE

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INTRODUCTION

For the volumetric determination of molybdenum a number of oxidimetric reagents, with which trivalent molybdenum can be determined by direct titration, molybdenum being oxidised either to Mo(V) or to Mo(VI), are recommended in the literature. It is of course necessary to reduce molybdenum to the trivalent form in a suitable way first. A short time ago the various methods of reduction, using either reductors[1] or amalgams[2] were dealt with in a review. Depending on the method employed to carry out the reduction, various forms of trivalent molybdenum may be prepared, their composition influencing not only for example the colour of the solutions obtained, but also their redox potential, stability etc. When studying the various forms of trivalent molybdenum in more detail, it was found[3] that its red form, of the probable composition[5] $M_3[MoCl_6]$ or $M_2[MoCl_5H_2O]$ (M = Na,K), obtained by reduction with a zinc amalgam in solutions containing more than 17% HCl is superior to the other forms with regard to stability, so that it can well be used for volumetric purposes[4]. For the redox potential of the system Mo(III)(red)/Mo(V) in 8 *N* HCl the value 0.266 V is given in literature[5].

In the present work we have studied the previously mentioned oxidation of the red form of Mo^{3+} by lead(IV) acetate, whose oxidative effects on other inorganic systems we have already studied earlier[6-9]. We have found that according to reaction conditions trivalent molybdenum may be oxidised quantitatively either to Mo(VI) or to Mo(V). This oxidation is so rapid, that it may be used even for direct potentiometric titration.

EXPERIMENTAL

Reagents

Hydrochloric acid, sulphuric acid and acetic acid (reagent grade, Lachema).

A solution of lead tetraacetate 0.1 *N* in glacial acetic acid (free from bivalent lead) was prepared by reaction of red lead (Pb_3O_4) with acetic acid[7] and its titer was determined by titrating with hydrazine sulphate[6].

A solution of trivalent molybdenum was prepared by dissolving the appropriate amount of MoO_3 (reagent grade, Merck) in 7 *N* HCl and reducing in an inert atmosphere by zinc amalgam[4]. The solutions obtained were stored in the reductor burette with zinc amalgam (see Fig. 1). The titer of the solution was controlled bichromatometrically[3].

Apparatus

The potentiometric titrations were carried out on an electronic pH-meter type EK/21 (Kovodružba, Prague) with indicating platinum and reference saturated calomel electrodes. (All potentials given further are expressed against the saturated calomel electrode.) For agitation of the mixture an electromagnetic stirrer or a stream of nitrogen were used. Titrations in an inert atmosphere were carried out in vessels commonly in use for such cases. For measuring the solutions officially calibrated glass-ware was used. For the titrations burettes of 25 ml volume with 0.1 ml divisions and of 5 ml volume with divisions of 0.01 ml were used. All Mo(III) titrations were carried out at room temperature.

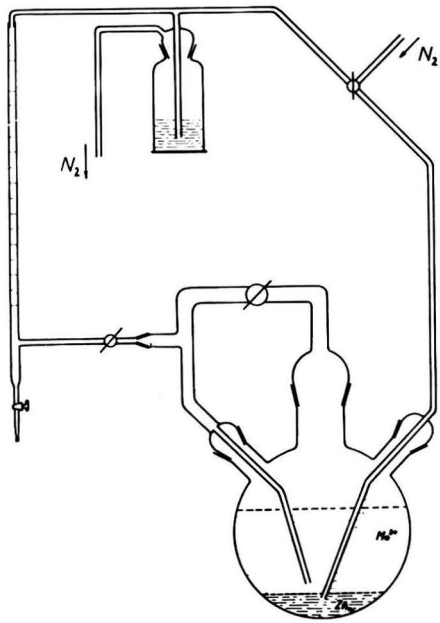

Fig. 1. Reductor burette (according to FIDLER[4]).

RESULTS

In the work presented we have found that the course of the oxidation of trivalent molybdenum by lead tetraacetate is greatly dependent on the hydrochloric acid concentration in the solution. The procedure used in our experiments was such, that solutions of varying hydrochloric or sulphuric acid concentration, containing 6 to 60 mg Mo in a volume of 50 ml were titrated in an inert nitrogen atmosphere at room temperature by a 0.1 *N* lead tetraacetate solution, using potentiometric control.

We have found that the oxidation of solutions acidified by sulphuric acid is very slow and also potential stabilisation of the indicating electrode is slow and cannot be influenced, not even by a change of the acidity of the solution. In solutions acidified

by hydrochloric acid the oxidation of trivalent molybdenum by lead tetraacetate is in all cases more rapid than in media of sulphuric acid; for direct potentiometric titrations it is however necessary that hydrochloric acid concentration in the solution should be at least 5 N.

In titrations of 5–7 N hydrochloric acid solutions two potential changes may be observed on the potentiometric curve (see Fig. 2), the first of which corresponds to the oxidation of Mo(III) to Mo(V), and the second to the oxidation to hexavalent molybdenum. The value of the first potential change increases with increasing con-

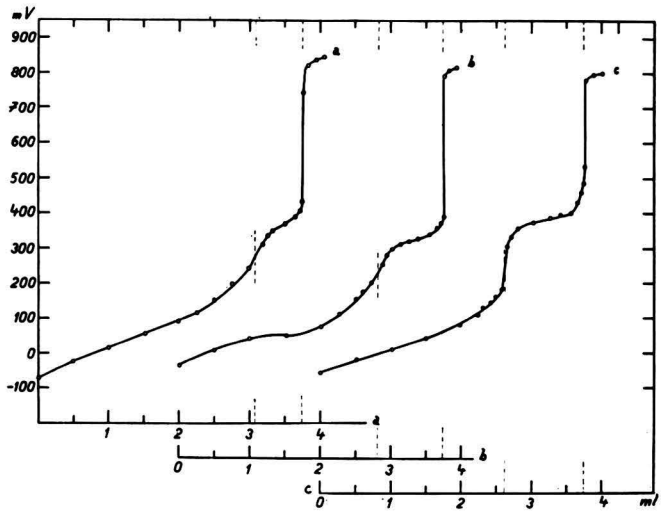

Fig. 2. Titration of 12.00 mg Mo(III) by 0.1 N lead tetraacetate in a volume of 50 ml: a, in 5 N HCl; b, in 6 N HCl; c, in 7 N HCl.

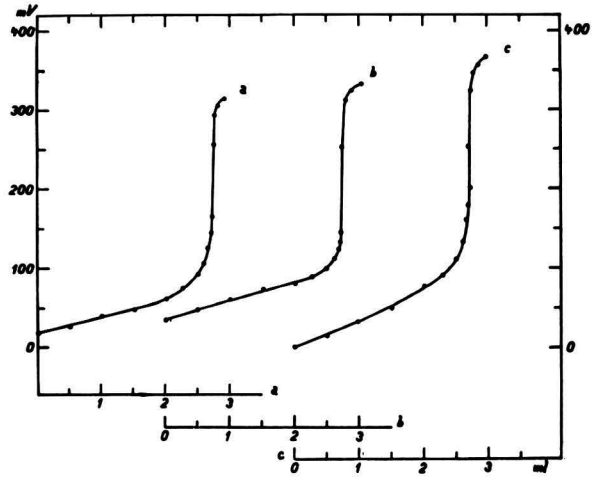

Fig. 3. Titration of 13.19 mg Mo(III) by 0.1 N lead tetraacetate in a volume of 50 ml: a, in 8 N HCl; b, in 9 N HCl; c, in 10 N HCl.

centration of the acid. The volume of reagent used in the first potential change decreases with increasing acid concentration, but even in 7 *N* HCl the volume found is higher than that corresponding to the quantitative oxidation of Mo(III) to Mo(V). The second potential change, whose value reaches a maximum in 6 *N* HCl corresponds in all the acidity range mentioned (5–7 *N* HCl) to the quantitative oxidation to Mo(VI) (see Table I).

TABLE I

TITRATION OF 12.00 mg Mo(III) (OXIDATION TO Mo(VI)) BY 0.1 *N* LEAD TETRAACETATE IN 50 ml 5–7 *N* HCl

Analysis	*HCl concentration (N)*	*Potential change for 0.01 ml (mV)*	*Inflexion potential (mV)*	*Amount given (mg)*	*Amount found (mg)*	*Deviation (%)*
1	5	300	580	12.00	12.02	+0.17
2	5.5	330	580	12.00	11.97	—0.25
3	6	390	600	12.00	12.00	0.00
4	6	375	610	12.00	11.96	—0.33
5	6.5	340	605	12.00	12.01	+0.08
6	7	280	655	12.00	11.96	—0.33
7	7	250	640	12.00	11.99	—0.08

TABLE II

TITRATION OF 24.25 mg Mo(III) (OXIDATION TO Mo(V)) BY 0.1 *N* LEAD TETRAACETATE IN 50 ml 8–10 *N* HCl

Analysis	*HCl concentration (N)*	*Potential change for 0.01 ml (mV)*	*Inflexion potential (mV)*	*Amount given (mg)*	*Amount found (mg)*	*Deviation (%)*
1	8	90	180	24.25	24.22	—0.12
2	8	80	200	24.25	24.24	—0.04
3	9	80	200	24.25	24.26	+0.04
4	9	105	195	24.25	24.28	+0.12
5	10	85	220	24.25	24.22	—0.12
6	10	75	230	24.25	24.25	0.00

When the titration is carried out in 8–10 *N* HCl solutions it is possible to titrate only to the first potential change (see Fig. 3) which in the medium given corresponds to the quantitative oxidation of trivalent to pentavalent molybdenum (see Table II). Further oxidation of Mo(V) by lead tetraacetate is very slow under the given conditions, so that direct potentiometric titration cannot be employed.

The results obtained on titrating 6–60 mg Mo in a volume of 50 ml with a 0.1 *N* lead tetraacetate solution in 6 *N* (oxidation to Mo(VI)) or in 9 *N* (oxidation to Mo(V)) hydrochloric acid are given in Tables III and IV.

From the results given in these tables it follows that for the determination of trivalent molybdenum by direct potentiometric titration with lead tetraacetate, oxidation to the hexavalent state (5–7 *N* HCl) as well as to the pentavalent state (8–10 *N* HCl) can be used. In the first case the potential change is greater than in the second, but it is necessary to wait 1–2 min for the stabilisation of the potential, whereas in the medium of 8–10 *N* HCl potential is stabilised immediately during the whole titration.

TABLE III

DETERMINATION OF Mo(III) IN A MEDIUM OF 6 *N* HCl

(1 ml 0.1 *N* $PbAc_4$ corresponds to 3.19833 mg Mo)

Analysis	*Amount given (mg)*	*Amount found (mg)*	*Deviation (%)*	*Potential change for 0.01 ml (mV)*	*Inflexion potential (mV)*
1	6.00	6.03	+0.50	380	580
2	6.00	5.97	—0.50	390	560
3	6.00	5.99	—0.17	365	530
4	12.00	12.02	+0.17	445	600
5	12.00	12.02	+0.17	410	575
6	12.00	11.96	—0.33	390	605
7	12.00	12.02	+0.17	410	615
8	12.00	12.02	+0.17	360	580
9	12.00	11.96	—0.33	385	610
10	12.00	12.02	+0.17	370	610
11	12.00	11.96	—0.33	340	590
12	12.00	11.99	—0.08	430	615
13	12.00	11.99	—0.08	340	610
14	60.00	59.93	—0.12	460[a]	600
15	60.00	59.98	—0.03	350[a]	580
16	60.00	60.07	+0.12	300[a]	630

[a] for 0.05 ml.

TABLE IV

DETERMINATION OF Mo(III) IN A MEDIUM OF 9 *N* HCl

(1 ml 0.1 *N* $PbAc_4$ corresponds to 4.7975 mg Mo)

Analysis	*Amount given (mg)*	*Amount found (mg)*	*Deviation (%)*	*Potential change for 0.01 ml (mV)*	*Inflexion potential (mV)*
1	24.25	24.23	—0.08	75	200
2	24.25	24.26	+0.04	100	220
3	24.25	24.23	—0.08	80	205
4	24.25	24.24	—0.04	75	210
5	12.12	12.11	—0.08	135	210
6	12.12	12.15	+0.25	100	205
7	12.12	12.13	+0.08	100	200
8	60.62	60.55	—0.11	175[a]	217
9	60.62	60.55	—0.11	150[a]	210

[a] for 0.05 ml.

SUMMARY

In solutions suitably acidified by hydrochloric acid it is possible to determine trivalent molybdenum by direct potentiometric titration using lead tetraacetate as the oxidimetric agent. In 5–7 *N* HCl solutions Mo(III) is quantitatively oxidised to Mo(VI), in 8–10 *N* HCl solutions to Mo(V).

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Short Communications

Separation of Inorganic Ions in Fused Salts by Electrophoresis on Glass Fiber Paper

In two earlier papers we described a number of separations of inorganic ions on strips of glass fiber paper with fused salts[1] or fused organic compounds as the eluant[2]. The aim of the present research is to examine the possibility of separating various inorganic ions, in a simple and fast way, by means of electrophoresis in fused salts, employing this paper as the support. In view of its chemical purity, uniform porosity and high resistance to heat and corrosion, we thought that glass fiber paper should offer advantages over the asbestos paper first employed by CHEMLA[3] and by ARNIKAR[4] in their work on isotope enrichment[3] and determination of the mobility of alkali and alkali earth ions[4] by electrophoresis in fused salts. As the fused medium the eutectics KNO_3–$LiNO_3$ (43 mole% $LiNO_3$, m.p. 132°) and KCl–LiCl (59 mole% LiCl, m.p. 352°) were chosen, respectively.

In order to simplify the experimental techniques, no special or accurate precautions were taken to ensure the complete dehydration of the eutectic LiCl–KCl, but we preferred to work at 450°[5]. Instead, the reproducibility of the method was controlled by employing different salts of the same ion in different experiments.

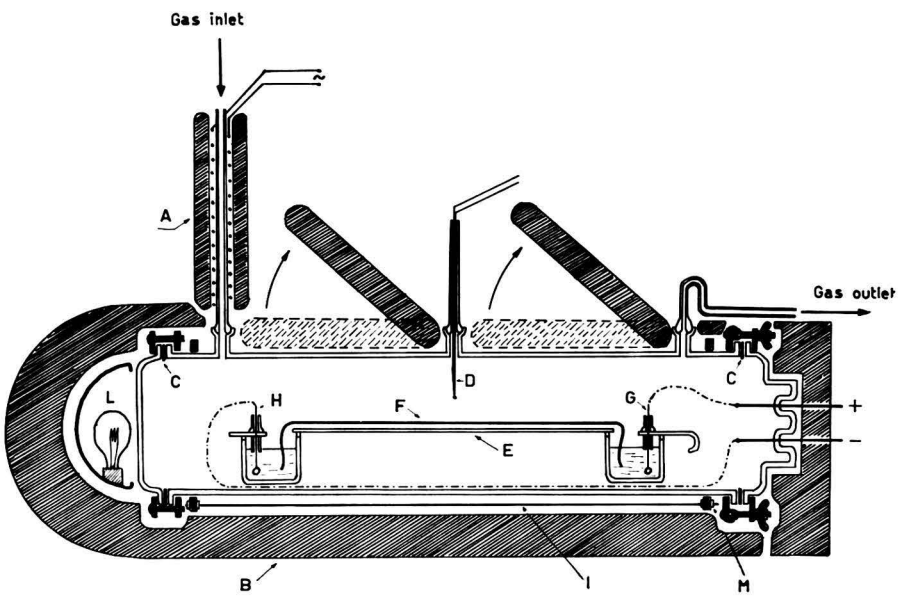

Fig. 1. Cross sectional view of the apparatus: A, preheating of gas stream; B, insulating jacket; C, Teflon lining; D, thermocouple; E, Pyrex glass plate; F, glass fiber paper strip; G, platinum anode; H, copper cathode; I, Ni–Cr heating wire; L, lamp; M, insulating porcelain; supports for Ni–Cr wire.

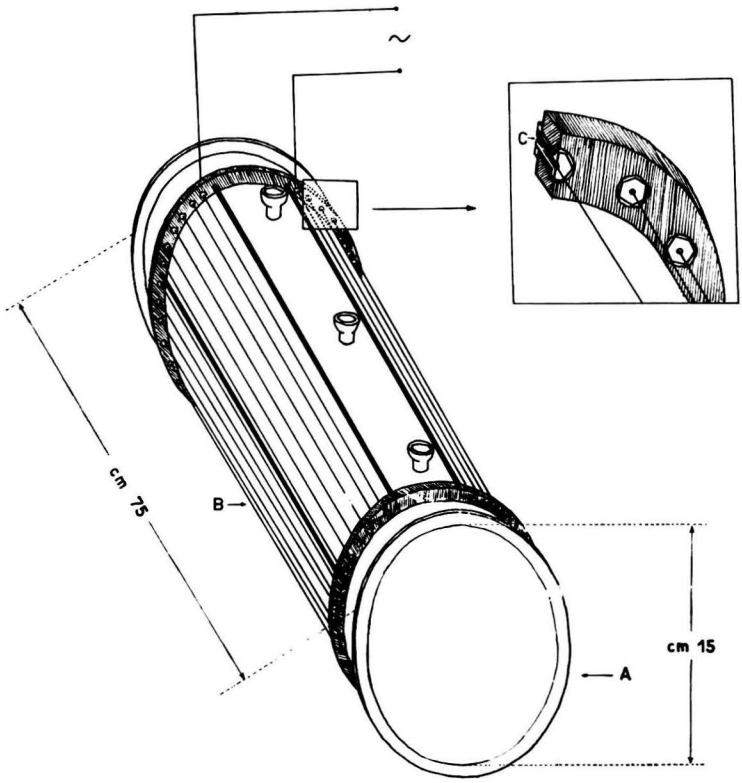

Fig. 2. View of the heating mantle: A, Pyrex glass cylinder; B, Ni–Cr heating wires; C, insulating porcelain supports for Ni–Cr wire.

EXPERIMENTAL

Electrophoresis is carried out in the Pyrex glass oven shown in Fig. 1. The oven is heated electrically by means of a nickel–chrome resistance wire as shown in Fig. 2, in such a way as to leave an ample window in the top of the oven. The temperature of the oven is maintained constant ($\pm 5°$) by means of a thermoregulator. Insulation is provided by asbestos material stuffed with glass wool. During operations a current of dry air is forced into the oven in order to remove the gases produced by electrolysis. If, however, an oxygen-free atmosphere is required, a current of dry nitrogen is sent through. In order to avoid cooling by the gas as it passes through, the gas stream is preheated before entry into the oven. The glass fiber paper employed (Whatman GB 0.65 mm thick; weight 150 g/m^2), was pretreated with HNO_3 (1 : 1) and washed three times with distilled water. The strip (0.5 $\times$ 56 cm) of this paper is impregnated uniformly with eutectic (120 mg/cm^2). After cooling, the strip is placed on a Pyrex plate welded directly onto the electrode vessel (see Fig. 1). From 100 to 500 μg of the ions under study are spotted onto the middle of the strip and the latter transferred to the oven. When the eutectic in the containers has melted properly, (this can be checked visually from the window at the top) the electrophoresis is begun and continued, at constant electric tension, for 4 h.

In the experiments carried out with the KNO_3-LiNO_3 eutectic, nitrates of the respective ions were employed, and in the experiments with the KCl–LiCl eutectic, the respective chlorides. The results obtained are shown in Table I. It can be seen that some separations are possible. This has been confirmed by us experimentally in certain separations such as Co–Pb–Ag and Zn–Cu.

TABLE I

MOVEMENT OF METAL IONS IN FUSED SALTS

	Distance (cm) moved in 4 h	*KCl–LiCl eutectic; t = 450°; 2 V/cm*	*KNO_3–$LiNO_3$ eutectic; t = 160°; 5 V/cm*
Anionic	3–0.5	Zn(II), Co(II)	
Isoelectric		Th(IV)	Th(IV)
Cationic	0.5–3	Ce(III)	Cd(II)
	3–5.5	Pb(II), Cd(II)	Pb(II)
	5.5–8	Cu(II)	Sr(II), Ba(II), Cs(I), Rb(I)
	8–10.5	Cs(I), Rb(I)	
	10.5–13	Na(I), Ag(I)	

In addition, in order to study the influence of the anion on the mobility of cations, a number of preliminary tests on the mobilities of Pb(II) and Cd(II) were made using different salts of these ions (Table II). These tests showed that the ions under examination exhibit the same mobility whichever of their salts is used.

TABLE II

MOVEMENT OF Cd(II) AND Pb(II) IN FUSED SALTS, WHEN EMPLOYED AS DIFFERENT SALTS

Salt employed	*Distance (cm) moved in 4 h*	
	KCl–LiCl eutectic; t = 450°; 2 V/cm	*KNO_3–$LiNO_3$ eutectic; t = 160°; 5 V/cm*
PbO	4.7	—
$PbCl_2$	4.8	4.6
$PbSO_4$	4.8	4.4
$Pb(NO_3)_2$	—	4.6
CdO	4.2	—
$CdCl_2$	4.4	—

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Differential Arrangement of Antimony Electrodes for pH-Measurement

Referring to the recent review on "*Electrodes for pH-measurements*" by BATES[1], I wish to recall the considerable body of research carried out at Strassbourg (France) by F. VLÈS and his pupils on differential pH-measurements with antimony electrodes and published between 1925 and 1935 in the "*Archives de Physique Biologique*"[2,3,4,5]. As this journal, which has since ceased to appear, is not easily accessible, it may be of interest to summarize the essential points of this convenient method.

1. A stick of metallic antimony about 3–4 cm long, and 2–4 mm diameter is obtained by fusing small pieces of pure antimony in a glass tube, in the luminous flame of a butterfly burner, and dipping the tube with the still liquid antimony into water at room temperature. The glass disintegrates, pieces of glass still adhering being removed mechanically. Only smooth, clean cylinders of antimony are used for manufacturing the electrodes.

2. A copper or brass wire, about 50 cm long, and 0.2–0.5 mm diameter is soldered in a small flame to both extremities of the antimony cylinder; the soldered joints are immediately insulated with wax or a wax–colophonium mixture.

3. Only then is the antimony cylinder broken into two pieces of approximately the same length; both are mounted (*e.g.* with wax–colophonium mixture) in glass tubes about 15 cm long, and of 3–5 mm internal diameter.

4. The measuring arrangement is shown in Fig. 1.

5. One calibration of the antimony electrodes per day, with three standard solu-

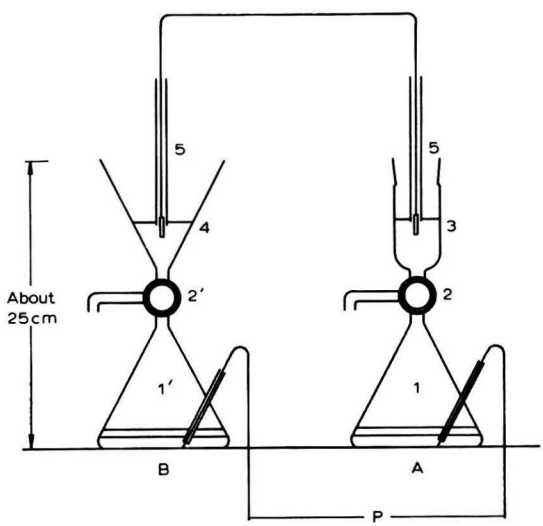

Fig. 1. VLÈS' arrangement for differential pH-measurement[2,3,4,5]; A, reference cell; B, measuring cell; P, potentiometer; 1, 1', Hg/calomel/satd. KCl soln. half cells; 2, 2', three-way stopcocks; 3, half cell for principal standard solution (0.1 *N* HCl); 4, measuring half cell; 5, antimony electrodes. The lateral inlet for satd. KCl soln. into the half cells 1, 1' is not shown.

tions (*e.g.* 0.1 *N* HCl and buffer salt solutions), is usually quite sufficient. The standard solutions are calibrated using a hydrogen electrode. The calibration curve of the antimony electrode is a straight line between pH 2 and pH 12; the error resulting from this procedure is less then 0.06 pH units (GEX[5], l.c., p. 125).

6. Before starting the measurements, the antimony electrodes are cleaned with an abrasive (powder, paper, or cloth), care being taken to treat the two electrodes in the same way; then the electrodes are rinsed with water. When they are not in use, both electrodes should be kept in contact, by crossing them as shown in Fig. 2.

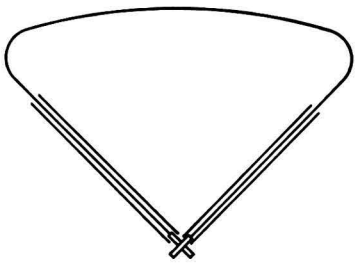

Fig. 2. Antimony electrodes in contact when not in use.

7. *Procedure*: cell A (half cell 3) is filled with 0.1 *N* HCl; cell B (half cell 4) is filled successively with: 0.1 *N* HCl (potential difference $p_0 = 0$), the other three buffer solutions for calibrating the electrodes (potential differences p_1, p_2, p_3), and finally the solutions to be measured. Before filling, cell B is rinsed each time with water and with the solution to be measured. The calibration curve is constructed from the measurements p_0, p_1, p_2, p_3.

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[1] R. G. BATES, *J. Electroanal. Chem.*, 2 (1961) 93.
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[3] F. VLÈS AND E. VELLINGER, *Arch. Phys. Biol.*, 6(1) (1927) 92.
[4] E. VELLINGER, *Arch. Phys. Biol.*, 7(2) (1928) 38.
[5] M. GEX, *Arch. Phys. Biol.*, 9(2) (1931) 110.

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Book Reviews

Transactions of the Symposium on Electrode Processes, by E. YEAGER, John Wiley & Sons, Inc., New York, and Chapman and Hall, Ltd., London, 1961, xiv + 374 pages, $20.

This well printed book contains the original text, complete with discussions, of all papers presented at the symposium of the theoretical electrochemistry division of the Electrochemical Society, held at Philadelphia on May 4th–6th 1959. Fourty-four participants presented eighteen papers covering nearly all aspects of this fundamental part of electrochemistry: *i.e.* the electrode processes. The authors of the papers are all active and well known scientists, so that this volume can be considered an up-to-date general survey of the whole field of the electrode processes.

J. Electroanal. Chem., 3 (1962) 288

Introduction to Semimicro Qualitative Analysis, 3rd. edn. by C. H. SORUM, Prentice Hall, Inc., Englewood Cliffs, N.J., U.S.A., 1960, vii + 209 pages, $3.75.

This is another book devoted to a practical course of qualitative analysis on the semimicroscale, now usually generally adopted because it saves time and material, and accustoms students to a cleaner and more precise experimental method. The treatment of the matter is the classical one: the usual 25 cations and 13 anions. The treatment of anions is less comprehensive than in other similar books and in fact, as an example, anions such as NO_2^-, $C_2O_4^{2-}$, AsO_3^{3-} are not identified.

The chapters devoted to the experimental part of the identification are preceded by a chapter of nearly 60 pages dealing with the theory of qualitative analysis, and with the various concepts necessary for its understanding: *i.e.* law of mass action, equilibrium, complex ions, pH, solubility and solubility product. All these concepts are dealt with in a very elementary way, as is necessary for beginners.

A good feature of this book is a collection of questions and problems which help to explain the theoretical concepts.

J. Electroanal. Chem., 3 (1962) 288

Handbuch der Laboratoriums-Destillation, by E. KRELL, 2nd. edn., Deutscher Verlag der Wissenschaften, Berlin, Germany, 1960, xiii + 526, D.M. 47.20.

A good indication of the usefulness of a book, particularly of a laboratory manual, is given when the first edition goes out of print in a relatively short time, and a new up-to-date edition appears very soon after the first one. This is the case with the Krell's book, the first edition appearing in 1958 and the second one three years later.

As in the first edition, the contents are divided and treated according to the usual description of a separation process. After an introduction (5 pages), a short history of distillation (10 pages) and a glossary of normalisation, units *etc.* (11 pages), the fourth chapter of nearly 160 pages is devoted to the theory of distillation, and to the experimental testing of distillation columns. The fifth chapter (nearly 100 pages) describes the different separation processes and considers as the most important points: quantity of substance, continuous or batch distillation, and temperature and pressure. In the sixth chapter (about 20 pages), the selection processes are relatively briefly treated. The three following chapters (altogether about 200 pages) are devoted to the technological aspects of distillation: different parts of a column, appropriate materials for construction, automation, measuring and controlling apparatus and, finally, how a laboratory distillation apparatus has to be assembled.

This book is very clearly written and well printed; its abundant and well drawn figures help considerably in understanding the text.

J. Electroanal. Chem., 3 (1962) 288

Semi-Micro Qualitative Analysis, by T. A. MUIR, Heinemann Ltd., London, 1961, iv + 44 pages, 3s.

This is a very short booklet of 44 pages written in the form of concise tables, to be followed in a practical course of qualitative analysis. In order to save time and materials the semimicroscale has been adopted, retaining the classical scheme of HCl, H_2S, NH_4OH, $(NH_4)_2S$, $(NH_4)_2CO_3$ and alkali groups for cations, whilst the analysis of anions is mentioned only briefly.

This booklet, as stated by the author, is intended for preparation of students for the examination for the General Certificate of Education, so that it has only a didactic interest.

Bearing this limitation in mind, the matter is described clearly enough for the required level, and this booklet can be considered a good help as a "bench handbook" to be consulted during the very simple analysis made at this level.

J. Electroanal. Chem., 3 (1962) 288

1. Fundamental electrochemistry

954 – Classification and nomenclature of electrochemical methods of analysis (in French). P. Delahay, G. Charlot and H. A. Laitinen (Chemistry Department, Louisiana State University, U.S.A., Faculté des Sciences, l'Université de Paris, France, and Chem. Dept., University of Illinois, U.S.A.). *J. Electroanal. Chem.*, 1 (1959/1960) 425–433.
A rational classification and nomenclature of electrochemical analytical methods with the exclusion of methods based on electrokinetic phenomena. Very few new terms are introduced and it is recommended that a few terms now found only occasionally in the literature should be dropped. [Authors]

955 – Membrane potentials. I. The theory of the e.m.f. of cells containing ion-exchange membranes (in English). G. J. Hills, P. W. M. Jacobs and N. Lakshminarayanaiah (Chemistry Department, Imperial College, London, S.W.7, Great Britain). *Proc. Roy. Soc.*, 262 (1961) 246–256.
A critical reformulation of both the theory of Teorell, Meyer and Sievers and the pseudo-thermostatic treatment of Scatchard for the membrane electric tension is made. The limitations of these two theories are discussed. Considering that diffusive processes across the membrane have been also described in terms of thermodynamics of irreversible processes, the authors also give a rigorous derivation of the expression for isothermal membrane electric tension. In the application of this last theory a more fundamental reference frame is adopted, which is the plane normal to the unidirectional fluxes passing through the system's centre of mass. [Su.Mo.Ce.]

956 – Membrane potentials. II. The measurement of the e.m.f. of cells containing the cation-exchange membrane, cross-linked polymethacrylic acid. G. J. Hills, P. W. M. Jacobs and N. Lakshminarayanaiah (Chemistry Department, Imperial College, London, S.W.7, Great Britain). *Proc. Roy. Soc.*, 262 (1961) 257–270.
The principal theories of membrane electric tension are tested by means of experimental data *e.g.* membrane electric tension, ionic transport numbers, solvent transport numbers, membrane composition and intra-membrane activity coefficient for the system: KOH(aq.)/polymethacrylate membrane/KOH(aq.). The lack of a good agreement between the experimental and calculated membrane electric tension shows that the existing theories are inadequate to calculate membrane electric tensions. Reasons for this failure are discussed and in the authors' opinion this matter requires further study. (See preceding abstract). [Su.Mo.Ce.]

957 – Kinetic equations for irreversible reactions in oscillographic polarography (in Russian). A. Ya. Gokhstein (Institute of Electrochemistry, Academy of Sciences, U.S.S.R.). *Doklady Akad. Nauk. S.S.S.R.*, 131 (1960) 601–604.
An equation is derived, expressing the maximum current by means of the rate constant and peak electric tension, which can always be measured on the oscillogram. The equation does not include terms for the rate of change of the electric tension and the diffusion coefficient, which are mostly unknown. The calculation is based on the fact that the ratio of concentration of the reacting substance in the electrode layer to its concentration in the mass of the solution is constant, and equal to 0.230. [Ot.So.]

958 – On the theory of *I–t* curves in the reduction of anions on a drop electrode with catalyst adsorption (in Russian). A. Ya. Gokhstein (Institute of Electrochemistry, Academy of Sciences, U.S.S.R.). *Doklady Akad. Nauk. S.S.S.R.*, 137 (1961) 345–348.
A purely theoretical treatment of the problem is stated, using a rather elaborate mathematical method. Various important quantities are derived mathematically, results being verified by calculations on data from other papers. [Ot.So.]

959 – On the impedance of galvanic cells. III. Applications to alternating current polarography (in English). Miss M. Rehbach and J. H. Sluyters (Laboratory for Analytical Chemistry, State University, Utrecht, The Netherlands). *Rec. trav. chim.*, 80 (1961) 469–482.
The d.c. dependence of the elements of the network described in part I (see abstract no. 807 *J.*

Electroanal. Chem., Abstracts Section, [4] 2 (1961)) is determined. The expressions are transformed and plotted in the complex admittance plane and three cases are discussed:
(a) where no electrode reaction occurs (the base line);
(b) for an electrode reaction with activation polarisation only;
(c) for an electrode reaction with diffusion polarisation only.
In the a.c. polarograms thus obtained, the base line is formed by a semi-circle, independent of the value of the double layer capacity. With a second semi-circle drawn through the top of the polarogram, both in the reversible and irreversible case, the construction furnishes the information necessary to calculate the quantities proportional to concentration.
The measurements can be performed for example by means of a simple a.c. bridge. In some cases a higher sensitivity is obtained by choosing some other frequency. Conversely, with known concentrations, the curves can be used for the determination of reaction rate and diffusion constants. [F.Vo.]

960 – Determination of ionic mobility in aqueous NaCl solutions at various temperatures (in Italian). V. Vitagliano (Institute of Physical Chemistry, University of Naples, Italy). *Gazz. chim. ital.*, 90 (1960) 1847.
Diffusion coefficients were determined interferometrically in NaCl (up to 5 *M*) at 0°, 18°, 35° and 50°. By using the activity coefficients and the transference numbers computed in a previous work (*Gazz. chim. ital.*, 90 (1960) 1839) the mobilities of both Na^+ and Cl^- were derived. [Fr.Pan.]

961 – Some regularities in the properties of strong electrolytes (in Russian). A. I. Gorbanev J. M. Kessler, J. M. Porarov and E. S. Sevostianov (Electrochemistry Institute, Academy of Sciences, U.S.S.R.). *Doklady Akad. Nauk S.S.S.R.*, 125 (1959) 1281.
Some important discrepancies between the Debye–Hückel limiting law and experimental results in the range of low concentrations (about 10^{-2} *M*) can be interpreted in different ways. On the other hand no connection between the discrepancies and the crystal radii of the ions can be found. [Ca.Cas.]

962 – The faradaic admittance of electrochemical processes. III. The frequency dependence. H. H. Bauer and P. J. Elving (Section of Agricultural Chemistry, Department of Agriculture, University of Sydney, Australia, and Department of Chemistry, University of Michigan, U.S.A.). *J. Electroanal. Chem.*, 2 (1960/1961) 53–59.
Recent experimental studies have demonstrated the inadequacy of proposed equations for the faradaic admittance, particularly in respect to the frequency dependence. Existing treatments of the faradaic admittance can give rise to two contradictory equations for the frequency dependence, equations being identical only at very low frequencies. The difference between these conflicting equations has a counterpart in the different behavior of two types of systems, which arises from the fact that either oxidation or reduction may be preferentially affected by polarisation effects. Previous experimental results on the variation of the faradaic admittance with frequency can be qualitatively interpreted on this basis. [Authors]

963 – Reference electrodes and tensions (in English). Giulio Milazzo and Giuseppe Bombara (Laboratorio di Chimica, Istituto Superiore di Sanità, Rome, Italy, and Laboratori Riuniti Studi e Ricerche (E.N.I.), S. Donato Milanese, Italy). *J. Electroanal. Chem.*, 1 (1959/1960) 265–284.
A critical review is made of problems, for which satisfactory solutions have not yet been obtained, relating to reference and comparison electrodes and tensions. The problems include: absolute electrode tensions; electric tensions relative to the standard hydrogen electrode; accuracy of the determination of the electric tension of hydrogen, silver/silver chloride and calomel electrodes; activity coefficients of single ionic species; diffusion electric tensions at liquid junctions between different solutions; isothermal and non-isothermal temperature coefficients of reference and comparison electrodes; problems of measurements in non-aqueous media.
The paper describes processes and methods that are being used in order to improve our present knowledge of these problems, and to bring their solutions nearer. In particular, for measurements at temperatures other than 25° and for those in non-aqueous media, the paper describes attempts which have been made to relate all measurements to a single reference electrode, *i.e.* to the single reference point on the scale of electric tensions as given by the standard hydrogen electrode, the electric tension of which is stated by definition to be equal to zero in water at 25°. [Authors]

964 – The a.c. polarographic wave. II. Height and shape at low and high frequencies. H. H. Bauer (Section of Agricultural Chemistry, Department of Agriculture, University of Sydney, Australia). *J. Electroanal. Chem.*, 2 (1961) 66–71.
The generalized equation for the a.c. polarographic wave has been used to examine the maximum

height, shape and width at half-height; explicit information about these quantities is given for the limiting cases at low and high frequencies.
1. At low frequencies, the height of the wave is very close to that predicted by earlier equations if the geometric mean of the diffusion coefficients is used in the latter formulation.
2. At high frequencies, the height of the wave depends markedly on the value of the transfer coefficient.
3. The wave is symmetrical about the summit electric tension at low frequencies; at high frequencies it is symmetrical only when $\alpha = 0.5$.
4. The width at half-height of the wave at low frequencies is almost independent of the relative values of the diffusion coefficients of the oxidized and reduced species. At high frequencies, the width depends markedly on the value of the transfer coefficient. The width is at least 50% greater at high frequencies than at low frequencies. [Author]

965 – Catalytic hydrogen waves of ethyleneiminobenzoquinone. I. Fundamental results of classical polarography (in German). H. Wagner and H. Berg (German Academy of Science, Berlin, and Institute of Microbiology and Experimental Therapy, Jena, Germany). *J. Electroanal. Chem.*, 1 (1959/1960) 61–72.
With ethyleneimino derivatives of *p*-benzoquinone exceptionally positive catalytic hydrogen waves were obtained, the properties of which were further characterized by means of classical polarography. On the basis of the results obtained and taking into consideration the conceptions of von Stackelberg and his school, an explanation for the special causes of this activity is proposed and the resulting possibility of investigating simultaneous adsorption is pointed out. [Authors]

966 – Microheterogeneous reduction catalysis in polarography (in German). H. Kapull and H. Berg (Institute for Microbiology and Experimental Therapy, Jena, and German Academy of Science, Berlin, Germany). *J. Electroanal. Chem.*, 1 (1959/1960) 108–132.
An investigation was made of the catalytic reduction of the electrode product R, which occurs during the electrode oxidation process. i–t curves obtained with a single drop were used to determine the dependence of this reaction on the half-wave electric tension $\pi_{1/2}$.
Palladium sol saturated with activated hydrogen was used as the reduction catalyst. The kinetics of the process can be calculated using the differential equations of Koutecky, Hans and Henke. Conclusions concerning the mechanism can be drawn from the relation between the velocity constant of the reduction and the electric tension:

$$\log K_j - \log K_i = B(\pi_{1/2j} - \pi_{1/2i})$$

Analysis of the i–t curves, using the simplified equation:

$$i = Kt^{\bar{\alpha}}$$

makes it possible to detect deviations due to the depolarizer and the range of the pseudo-monomolecular microheterogeneous reaction. [Authors]

967 – Dependence of oxidation electric tensions of permanganate, chlorate, bichromate-chromate and hydrogen peroxide solutions on pH (in Russian). I. E. Flis and M. K. Binyaeva (Leningrad Technological Institute, Leningrad, U.S.S.R.). *Zhur. Fiz. Khim.*, 35 (1961) 1003–1009.
The dependence of the oxidation electric tensions of platinum and gold electrodes in the above-mentioned solutions on pH was investigated. It is shown that the oxidation electric tension does not correspond to the equilibrium state as is the case with hypochlorite, chlorite and ClO_2 solutions. It is suggested that the main factors determining the oxidation electric tension of such systems are the rate of irreversible decomposition of the oxidising agent in the solution, resulting in formation of oxygen, and the thermodynamic state of oxygen on the electrode surface. [Ot.So.]

968 – An application of the Fuoss–Onsager conductance theory to the alkali halides in several solvents. Robert L. Kay (Metcalf Research Laboratory, Brown University, Providence, Rhode Island, U.S.A.). *J. Am. Chem. Soc.*, 82 (1960) 2099–2105.
The solution of the Fuoss–Onsager conductance equation for associated and unassociated electrolyte data has been adapted to computer calculation. Conductance data for the alkali halides in several solvent systems has been analyzed. The ionic size parameter, a, varies in the expected manner for the different electrolytes, but its magnitude is smaller than that expected. This is explained on the basis of association constants for these electrolytes. [R.W.Mu.]

969 – Der Ionenaktivitätskoeffizient von Caesiumchlorid in Beziehung zu der Dielektrizitätskonstante der Lösung (in Deutsch). S. Kilpi (Chemisches Institut der Universität, Helsinki, Finland). *Suomen Kemistilehti*, 32 (1959) B 125–127.

Es wird die Abhängigkeit des Ionenaktivitätskoeffizienten des CsCl von der Konzentration in Beziehung zu der Dielektrizitätskonstante der Lösung betrachtet. Wie es bei Chlorwasserstoff der Fall war, nähert sich die Dielektrizitätskonstante der Lösung bei steigender Konzentration dem Wert der Dielektrizitätskonstante des Elektrolyten, im vorliegenden Fall der Dielektrizitätskonstante des festen Salzes. [St.Bre.]

See also abstracts nos. 1104, 1107, 1108, 1157, 1208, 1209, 1210, 1227, 1253, 1255, 1256.

2. Apparatus and accessories

970 – Zeroing of direct current amplifiers. R. W. Tolmie (Atomic Energy of Canada Ltd., Ottawa, Canada). *Rev. Sci. Instr.*, 30 (1959) 205–206.
Some amplifiers can be modified so that they can be zeroed by simply depressing, and then releasing, a switch. When the switch is released a signal is applied to the input, which is just adequate to reduce the output voltage to zero. An example is given of a simplified circuit diagram of a Tracerlab SU 1 H radiation meter. [G.Mar.]

971 – High current electronic potentiostat. D. N. Staicopoulos (Engineering Research Laboratory, E. I. du Pont de Nemours & Co., Wilmington, Delaware, U.S.A.). *Rev. Sci. Instr.*, 32 (1961) 176–178.
The potentiostat described comprises essentially a high input impedance d.c. amplifier, a low impedance transistorized d.c. amplifier and a transistorized current amplifier, connected in a bridge arrangement. The prototype is capable of delivering high currents (up to 5 A for anodic or cathodic polarization) at minimum delay and at controlled values of the electric tension of the electrodes. [G.Mar.]

972 – The self-acting elimination of the impoverishing effect by means of intermittent polarography (in German). M. Becker (Göttingen, Germany). *Angew. Chem.*, 73 (1961) 495.
(A summary of the lecture held at the 60th meeting of the Bunsen Society for Physical Chemistry).
Um den Verarmungseffekt, der einen bedeutenden Fehler verursacht bei der polarographischen Diffusionskoeffizient- und Reaktions–Geschwindigkeitskonstante–Bestimmungen, eliminieren zu können, wurde ein Polarograph konstruiert, der selbsttätig durch periodische Unterbrechung der Elektrolyse dafür sorgt, dass bei Tropfenbeginn die Konzentration des Depolarisators an der Elektrodenoberfläche hinreichend genau gleich der Konzentration im Innern der Lösung ist. So braucht man keine mechanische Regelung der Tropfzeit. Der Einfluss des Rückdrucks und des Spüleffekts wurde durch Verwendung geeigneter weiter, im mittleren Teil verengter Zylinderkapillaren ausgeschalten. So erreicht man bei den absoluten polarographischen Bestimmungen eine Genauigkeit von 2–3%. [Ja.Inc.]

973 – Oscilloscopic polarography. III. Half-wave electric tensions with superimposed a.c. circuit (in Spanish). A. Rodriguez and J. Sancho ("Rocasolano" Murcia, Spain). *Anales real soc. españ. fis. y quim. (Madrid)*, 57 B (1961) 349–352.
A detailed description of an improved a.c. polarograph circuit, using a 6H6 diode as square–wave tension generator is given. The instrument is provided with an "equivalent" RC circuit which can replace the cell and reveals possible artefacts unrelated to the electrode process under study. [L.Gi.]

974 – Oscilloscopic polarography. IV. Quantitative measurements (note) (in Spanish). A. Rodriguez, J. G. Hurtado, J. Menchon and J. Sancho ("Rocasolano" Murcia, Spain). *Anales real soc. españ. fis. y quim. (Madrid)*, 57B (1961) 411–414.
Currents corresponding to the base, median and peak of conventional polarographic waves are determined by a compensation method using an a.c. oscilloscope as null instrument. The vertical amplifier input is alternately connected, with the help of a mechanical vibrator, to an adjustable electric tension derived from a precision potentiometer, and to a sampling resistance in series with the cell. The measurements are made as the drop falls. [Li.Gi.]

975 – Support for Jones–type conductance cell (in English). K. B. Morris and W. W. Baker (Air Force Institute of Technology, Wright-Patterson A.F.B., Ohio, U.S.A.). *Chemist Analyst*, 50 (1961) 86.

On décrit un support en matière plastique qui est destiné à soutenir les cellules de conductimétrie dans les bains thermostatiques où on les plonge.
Les détails de réalisation sont donnés pour un modèle reçevant les cellules Jones de toutes dimensions ainsi qu'un type de cellule Shedlovsky. [J.Des.]

976 – Electrode washing assembly for routine pH determinations (in English). F. Sue Lee and O. Nowakowski (Water Service Laboratories Inc., New York, N.Y., U.S.A.). *Chemist Analyst*, 50 (1961) 80.
Les auteurs décrivent un appareillage pour soutenir un bécher de détermination de pH et pour rincer l'électrode de verre. Le seul matériel nécessaire consiste en une bouteille de polythène et un tube de caoutchouc. [J.Des.]

977 – Device for the simultaneous turning-on of stopwatch and current (in Russian). P. N. Nikolaev and G. P. Timofeev (State University, Gorkii, U.S.S.R.). *Zhur. Fiz. Khim.*, 35 (1961) 1860–1861.
A device is proposed for simultaneously turning on the stopwatch and the current. It consists of a modified package switch and the stopwatch. A turn of the switch dial actuates a lever pressing on the crown of the watch so that the latter is turned on together with the current. The device was tested with the aid of a recording chronograph, and it was found that the error of measurement does not exceed 0.1 sec for each 10 min. [Ot.So.]

978 – Potentiostat for electrochemical investigations (in Russian). V. S. Borovkov and S. B. Averbukh (Mendeleev Institute of Chemical Technology, Moscow, U.S.S.R.). *Zhur. Fiz. Khim.*, 35 (1961) 1867–1869.
A potentiostat has been devised for electrochemical investigations, in which use is made of domestic instruments and devices, including a P–4 potentiometer, an EU–109 alternating current amplifier and chopper, and a reversible motor RD–09. For automatic recording of current passing through the cell, use is made of an electronic potentiometer EPP. [Ot.So.]

979 – The determination of small and medium losses of liquids with an unslotted coaxial line (in German). Hans Wirth (Institute for the Development of Physico-chemical Analytical Methods, Weilheim/Obb., Germany). *Mitt. Inst. Entwicklung chem.-physik. Analysenmeth., Weilheim/Obb.*, 1 (1961) 1–4.
Für eine beidzeitige abgeschlossene Koaxialleitung werden für den Resonanzfall die Auswertungsgleichungen gegeben. Eine vereinfachte Methode liefert die relative Dielektrizitätskonstante ε' und den dielektrischen Absorptionskoeffizienten ε''. Für die analytische Anwendung der Messung von Debye-Verluste ist die hier beschriebene einfache Auswertung von Bedeutung. [Fr.Oe.]

980 – A simple microcoulometric arrangement for polarographic purposes using the three-electrode system (in English). J. Masek (Polarographic Institute, Czechoslovak Academy of Sciences, Prague, Czechoslovakia). *J. Electroanal. Chem.*, 1 (1959/1960) 416–421.
A simple microcoulometric arrangement for polarographic purposes has been designed using a three-electrode system. As a working anode, a graphite pencil was used. The arrangement was tested experimentally on irreversible systems and satisfactory results were obtained. Possible sources of errors involved in performing the microcoulometric measurements were discussed. [Author]

981 – A conductometric technique for the continuous control of flowing mixtures (in Spanish). J. Ocon and M. Lamela (A. de G. Rocasolano, Santiago de Compostela, Spain). *Anales real soc. españ. fis. y quim. (Madrid)*, 57B (1961) 77–81.
The technique is based on the oscilloscopic measurement of the variation of the a.c. voltage drop across the output of a low-frequency generator, consecutive to its loading by the conductometric cell. Calibration curves are given for the acetic acid–water and methanol–benzene systems, chosen as examples. [L.Gi.]

982 – A new immersion cell with adjustable cell factor (in German). F. Oehme (Institute for the Development of Physico-chemical Analytical Methods, Weilheim/Obb., Germany). *Mitt. Inst. Entwicklung. chem.-physik. Analysenmeth., Weilheim/Obb.*, 1 (1961) 12–13.
Die unerlässliche Voraussetzung für alle direkt anzeigenden Leitfähigkeitsmessgeräte, eine Messzelle der Zellenkonstante $k = 1.00$ verfügbar zu haben, wird auf einem neuen Weg erreicht. Durch Verschieben des eigentlichen Elektrodenträgers in einem sich nach unten konisch verjüngendem Rohr kann das Randfeld der Messstrecke in wählbarer Weise beschnitten werden. Es genügt eine relativ grobe Fertigung der geometrischen Abmessungen der Messstrecke, da Abgleichtoleranzen von $\pm$ 10% der Zellenkonstanten vorliegen. [Author]

983 – Ionophorèse et chromatographie ionophorétique en couche mince (en allemand). C. G. Honegger (Laboratoire de la Policlinique Neurologique, Universitaire, Bâle, Suisse). *Helv. Chim. Acta*, 44 (1961) 173.
L'auteur présente une méthode de séparation par ionophorèse en couche mince sur plaque de verre. Il améliore le pouvoir séparateur par la mise au point d'un processus à deux dimensions: combinaison de l'ionophorèse et de la chromatographie. La description de l'appareillage est accompagnée d'un schéma.
Comme adsorbant dans le cas des amines et des acides aminés, il utilise le "Kieselgel G'", le "Kieselgur G'" et l'alumine G' pour la méthode simple et le "Kieselgel G'" pour le procédé à deux dimensions. La séparation est au moins aussi bonne que celle qu'on effectue sur papier.
[De.Mo.]

984 – Electrodes of sodium–barium silicate glasses for pH measurements (in Russian). G. T. Petrovski and F. Čůta (Department of Special Analytical Methods, Institute of Chemical Technology, Prague, Czechoslovakia). *Collection Czechoslov. Chem. Communs.*, 26 (1961) 2289–2297.
The influence of the composition of sodium–barium glass on its ability to indicate hydrogen ion concentration was investigated. The results were tabulated as the dependence of glass composition and pH at which the sodium error is 10%. The least sodium error was found for a glass of the composition 14–17.5 mole % Na_2O and 7.5–10 mole % BaO, its electric tension being linearly dependent on pH up to pH 13.5. [Ot.So.]

985 – Construction of dual gold polarised electrodes (in English). H. Huth and N. C. Johnson (School of Medicine, Washington University, St. Louis, Mo., U.S.A.). *Chemist Analyst*, 50 (1961) 55–56.
Pour fabriquer une double électrode d'or les auteurs utilisent, ici, un verre à base d'uranium qui fond à la fois plus bas que le métal et que les soudures à l'argent couramment utilisées. En outre ce verre est susceptible de se coller auz verres borosilicatés normaux. On peut ainsi fixer dans un tube de verre (1.5 cm de diamètre) deux fils d'or (1.5 cm de long). [J.Des.]

986 – Use of a rotating disk electrode with ring for investigation of intermediate products in electrochemical reactions (in German). A. Frumkin, L. Nekrasov, B. Levich and Iu. Ivanov (Electrochemical Laboratory, University of Moscow, and Institute of Electrochemistry, Academy of Sciences, Moscow, U.S.S.R.). *J. Electroanal. Chem.*, 1(1959/1960) 84–90.
A rotating disk electrode fitted with an isolated metal ring was found to be a suitable instrument for investigating intermediate products in electrochemical reactions. Starting from the theory of convection diffusion, equations were deduced and these were tested in the case of the reduction of oxygen in alkaline solution. [Authors]

987 – Apparatus for high pressure polarography. W. B. Schaap, R. F. Conley and F. C. Schmidt (Indiana University, Bloomington, Ind., U.S.A.). *Nuclear Sci. Abstr.*, 15 (1961) 652, *Abstr. No.* 5043. [Red.]

988 – Compensation for temperature variations within the cell of a dissolved oxygen indicator/recorder incorporating a wide-bore dropping mercury electrode. A. Littlewood (Department of Scientific and Industrial Research, Warren Spring Laboratory, Stevenage, Herts., Gt. Britain). *Analyst*, 86 (1961) 359–360.
In the method of Briggs, Dyke and Knowles, a wide-bore dropping mercury electrode was maintained at a constant electric tension with respect to a zinc anode, when the cell current was a measure of the oxygen content. This paper describes a thermistor sensing device which automatically compensates for changes in current caused by changes of cell temperature. Mathematical expressions are derived for values of circuit components. [P.O.Ka.]

989 – Electrical conductance cell assembly for precise measurements with carbonates, oxides and fluorides up to 1000°C. G. J. Janz and M. R. Lorenz (Rensselear Polytechnic Institute, Department of Chemistry, Troy, New York, U.S.A.). *Rev. Sci. Instr.*, 32 (1961) 130–133.
In this communication a conductance cell assembly is described, with a capillary, which permits precise electrical conductance measurements with high precision standard bridge circuits, such as the Leeds & Northrup "Jones" bridge. The capillary is machined from a single crystal of magnesium oxide, MgO, a refractory relatively inert and insoluble in carbonates, oxides and fluorides. The various other components of the cell that are in contact with the molten salts are made of gold or

gold–palladium alloy, thus allowing the use of this cell at temperatures up to 1000°. The capillary can be easily removed from the assembly for cleaning.
Results reported show that the data for molten KCl and molten KNO_3 may be used as high temperature conductance standards for the calibration of such cells. [G.Mar.]

990 – Simple electronic arrangement for the coulometric determination of small amounts of carbon in steel (in Czech). J. Hejduk and E. Rechziegel (Physical Institute, Czechoslovak Academy of Sciences, Prague, Czechoslovakia). *Chem. listy.*, 55 (1961) 1062–1067.
A simple electronic instrument is described, of sufficient stability for coulometric determination of carbon in steel and other metals, and for the determination of small amounts of carbon also in other materials, in which carbon can be oxidised to carbon dioxide. Carbon dioxide is titrated by barium hydroxide, generated electrolytically from barium chloride. Indication is potentiometric by means of a platinum indicating electrode compared to a saturated calomel electrode. The amount of electric current consumed is calculated from current intensity and time of its passage through the absorbing solution. A wiring diagram, and detailed descriptions and examples of results are included. [Ot.So.]

991 – Derivative potentiometric titrations with tantalum and niobium electrodes (in German). Friedrich Oehme (Institute for the Development of Physico-chemical Analytical Methods, Weilheim/Obb., Germany). *Mitt. Inst. Entwicklung. chem.-physik. Analysenmeth., Weilheim/Obb.*, 1 (1961) 22–24.
Nach einer kurzen Begründung der Vorteile, welche die Aufnahme von Titrations-Diagrammen nach der Methode der 1. Ableitung bringen, wird auf die schaltungstechnischen Besonderheiten kurz eingegangen. Von besonderem Interesse ist, dass Tantal- und Niob-Elektroden bei Strombelastung anodisch eine Oxydschicht ausbilden, welche im Zusammenwirken mit einem äusseren Widerstand im Messkreis die Funktion des differenzierenden Kondensators übernimmt. Auf die verschiedenen sich daraus ergebenden Messmöglichkeiten wird kurz eingegangen. [Author]

992 – Electrical conductivity of dilute aqueous phosphate solutions and phosphoric acid at elevated temperatures and pressures (in English). G. Whitehead (Department of Chemical Engineering, The University, Sydney, Australia). *J. Appl. Chem.*, 11 (1961) 136–140.
The construction of a combined pressure and conductivity cell suitable for pressures up to 16 atm. and temperatures up to 200° is described. Each compound attained a maximum conductivity, and then decreased with increasing temperature. The temperatures of the conductivity maxima were lower than those previously reported for uni- and divalent salts. [D.S.Ru.]

993 – Voltammetry in liquid sulfur dioxide. I. Technique and theoretical problems. P. J. Elving, J. M. Markowitz and I. Rosenthal (Department of Chemistry, University of Michigan, Ann Arbor, Mich., U.S.A.). *J. Phys. Chem.*, 65 (1961) 680–686.
The use of the non-protonic solvent, sulfur dioxide, as a medium for voltammetry and polarography has been considered. Apparatus and procedures for various solutes are described using two indicating electrodes, a dropping mercury electrode and a stationary cylindrical platinum electrode and two comparison electrodes, a mercury calomel pool and a silver–silver chloride electrode. [D.S.Ru.]

994 – Use of polyethylene as electrode sealer (in English). R. C. Sheridan (University of Kentucky, Lexington, Ky., U.S.A.). *Chemist Analyst.*, 50 (1961) 86.
L'utilisation de la pâte obtenue en ramollissant au dessus d'une flamme mince, de petits morceaux de polythène, permet de sceller facilement l'argent au verre. [J.Des.]

995 – Combined agar gel–paper electrophoresis (in English). B. Zak, F. Volini, J. Briski and L. A. Williams (Department of Pathology, Wayne State University, College of Medicine, Detroit, Mich., U.S.A.). *Am. J. Clin. Pathol.*, 33 (1960) 75–82.
Serum proteins or haemoglobins can be separated and estimated by a new method of electrophoresis on agar-gel. The separation can be achieved in 25–45 min. Up to 5 different protein zones can be separated, and the elution recovery is similar to that obtained by the Spinco procedure. Wet paper is laid on a glass plate and molten agar is layered on it between two glass rods. After electrophoresis, the gel and paper are dried together, and in this way the protein bands are concentrated on the paper surface. The subsequent staining gives sharp definition of zones. [Gio.Ser.]

See also abstracts nos. 1001, 1217, 1226, 1246.

3. Polarography

996 – Effect of viscosity of the media on the half wave potential and the diffusion current in polarography (in English). S. N. Mukherjee, A. M. Gosh and A. Chakravarti (Judavpur University, Calcutta, India). *J. Sci. Ind. Research* (India), 20B (1961) 77.
The effect of varying the viscosity of the medium on the half wave electric tension and diffusion current has been studied with reference to Cd and Zn as the reducing ions; glycerine, in amounts varying from 12 to 90%, was added to the medium to vary its viscosity. The relation $i_d\eta^{\frac{1}{2}}$ = constant (η is coefficient of viscosity) was found to hold throughout the entire range of viscosity of the medium investigated. [R.S.Sa.]

997 – Alternating current polarography and tensammetry. H. H. Bauer (Section of Agricultural Chemistry, Faculty of Agriculture, University of Sydney, Australia). *J. Electroanal. Chem.*, 1 (1959/1960) 363–378.
Review illustrating principles, apparatus, scope and results of a.c. polarography. Characteristic features of tensammetric waves as applied to the investigation of reaction mechanisms and to analytical purposes are discussed. A table with the values of summit electric tensions *versus* S.C.E. is given. [Red.]

998 – Polarographic studies of radioactive isotopes. W. B. Schaap and E. Wildman (Indiana University Foundation Research Division, Bloomington, U.S.A.). *Nuclear Sci. Abstr.*, 15 (1961) 652, *Abstr. No.* 5042. [Red.]

999 – The theoretical shape of the titration curve in amperometry with two indicator electrodes (in English). H. L. Kies (Laboratory for Analytical Chemistry, Technical University, Delft, The Netherlands). *J. Electroanal. Chem.*, 1 (1959/1960) 171–175.
In order to ascertain the influence of certain factors (E, R) on the shape of the titration curve, it is desirable to define the relative current intensity j as $j = i/i_{1/2}$.
The angle of the slope of the part of the titration curve near the equivalence-point varies between 71.5° and 90° when the applied voltage is 59 mV; this angle increases with the resistance. A small equilibrium constant causes an appreciable current intensity at the equivalence-point.
The formulae are not suitable for calculating the influence of the applied voltage on the course of the titration in the vicinity of the equivalence-point. [Author]

1000 – Analytical applications of alternating-current cyclic voltammetry. Andre L. Juliard (Houdry Process Corp., Linwood, Pa., U.S.A.). *J. Electroanal. Chem.*, 1 (1959/1960) 101–107.
Reproducible a.c. polarograms with a platinum electrode, are obtained when the polarization voltage is scanned cyclically between —1.0 and +1.5 V *vs.* S.C.E., at a rate intermediate to that of conventional and oscilloscopic polarography. These polarograms are useful for analytical determinations of compounds oxidizable or reducible at electric tensions more positive than that of the dissolution of mercury.
The shapes of these polarograms are determined much more by chemical changes occurring close to or at the surface of the electrode than by physical transfer through the diffusion layer, even when highly electroactive particles are involved. [Author]

1001 – The bubbling platinum electrode (in English). Danilo Cozzi and Pier Giorgio Desideri (Analytical Chemistry Institute of Trieste and Florence, Italy). *J. Electroanal. Chem.*, 1 (1959/1960) 301–306.
The authors present, and give examples of, the use of a new type of platinum electrode, the bubbling platinum electrode, which may be used in place of the dropping mercury electrode for the study of the electrochemical properties of substances with high redox electric tensions. [Authors]

1002 – Investigation of capacity phenomena using methods derived from classical polarography (in German). R. Kalvoda (Polarographic Institute, Academy of Science, Prague, Czechoslovakia). *J. Electroanal. Chem.*, 1 (1959/1960) 314–323.
In this paper the polarographic method with superimposed alternating voltage (according to Breyer) has been compared both with oscillographic polarography using alternating current and alternating voltage, and also with classical polarography, by means of an investigation of a series of compounds which are adsorbed on the mercury electrode. Similar results were obtained for these methods, all of which showed dependence of the differential capacity, or one of the values related to it, upon the electric tension. [Author]

1003 – L'emploi du polarographe oscillographique en microbiologie (en allemand). D. Kalab (Bioveta, Ivanovice na Hané, Tchécoslovaquie). *Experientia*, 17 (1961) 275.
L'auteur utilise le polarographe oscillographique P-524 à courant alternatif à goutte de mercure pour l'étude du comportement et du métabolisme de quelques acides aminés, purine, pyramidine, etc. dans diverses conditions et pour diverses cultures microbiologiques. Il étudie aussi l'activité de certains enzymes (asparaginase nucléodesaminase).
L'auteur donne un oscillogramme que montre la déformation que subit la courbe lorsqu'on passe de solutions renfermant l'adénine sans Escherichia. [De.Mo.]

1004 – Influence of ohmic resistance and of double layer capacity on peak current in a.c. polarography (in German). H. Schmidt and M. von Stackelberg (Physical Chemistry Institute, University of Bonn, Germany). *J. Electroanal. Chem.*, 1 (1959/1960) 133–142.
The well-known fact that with increasing frequency the height of the peak current decreases after reaching a maximum, was hitherto explained by assuming that the electrode reaction could not follow the rapid changes of the electric tension. The decrease of the peak current also occurs, however, in the case of reversible reactions. This can be attributed to the fact that on keeping the alternating electric tension constant, the effective alternating electric tension at the electrodes decreases with increasing frequency. Mathematical treatment of the problem shows that the ohmic resistance of the circuit and the double-layer capacity of the electrode are responsible for this decrease in the peak current.
In square wave polarography the impedance of the measuring circuit determines the time constant and is therefore responsible for the degree of elimination of the capacity current.
[Authors]

1005 – Position of polarograms obtained at solid electrodes in current–voltage–time coordinates (in Russian). Yu. K. Delimarsky and A. V. Gorodisky (Institute of General and Inorganic Chemistry, Academy of Sciences, U.S.S.R.). *Zhur. Fiz. Khim.*, 35 (1961) 1091–1094.
Polarization processes at stationary electrodes have been investigated. The automatically recorded polarograms have been shown to coincide with a surface $F(i,U,t)$ plotted on the basis of the time–current curves. Different methods of solid electrode polarography are interpreted with the aid of the $F(i,U,t)$ function. [Ot.So.]

1006 – Polarographic maxima and solution movements (in English). W. M. MacNevin and S. R. Steele (Department of Chemistry, Ohio State University, Columbus, Ohio, U.S.A.). *Anal. Chim. Acta*, 24 (1961) 381–385.
The present paper presents additional information describing the phenomenon of motion associated with polarographic maxima and contributes to the existing theories of maxima. Upward motion is only observed with maxima occurring on the negative side of the electrocapillary zero, but both upward and downward motion occur with positive maxima. Such motion may occur during the life of a single drop.
The study of the two ions $Fe(CN)_6^{3-}$ and Cu^{2+} shows that a critical ratio of concentration to growth rate exists, below which upward motion prevails and above which downward motion prevails.
The negative character of the mercury surface as it leaves the glass capillary, the time interval for the mercury surface to lose its negative orientation and the attraction of the ions of the solution by the non-uniformly charged surface, are the principal factors of motion. [P.Me.]

1007 – Electron resonance and photopolarography (in German). H. Berg (Jena, Germany). *Angew. Chem.*, 73 (1961) 495.
(A summary of the lecture held at the 60th meeting of the German Bunsen Society for Physical Chemistry).
Die während der Bestrahlung von Ketonen in gepufferten isopropanol-haltigen Lösungen gebildeten Radikale, (R) $\dot{C}$ — OH lassen sich bis zu Konzentrationen von $10^{-6}M$ herab polarographieren. Im Fall langlebiger Ketyle (aus Perinaphthenon) wird die reversibele Oxydationsstufe mit einer Empfindlichkeit von $2 \cdot 10^{-9}$ A/mm, oder die zeitliche Änderung des Radikalgrenzstromes bei konstanter Spannung registriert. Im Fall kurzlebiger Ketyle (aus Benzoin, in schwach alkalischem Medium) registriert man im Verlauf weniger i–t–Kurven. Zur Ausführung der Messungen verwendete man Spitzkapillare (um den Verarmungseffekt zu vermindern) und schnellschwingende Stylo-Galvanometer.
Bei Dauerbestrahlung der Ketone wird die Registrierung durch photokinetische Ströme beeinflusst, und das Radikal unterliegt ausser seiner "Dunkelreaktion" auch einer Photoreaktion. Nach der Blitzreduktion hingegen kann die Dunkelreaktion 2-Ordnung potentiostatisch verfolgt werden. Photopolarographie hat Vorteile gegenüber Elektronenresonanz und Kurzzeitspektroskopie, wenn es sich um Lösungen mehrerer stark absorbierender Komponenten handelt. [Ja.Inc.]

1008 – Faradaic admittance of electrochemical processes (in English). S. K. Rangarajan and K. S. G. Doss (Central Electrochemical Research Institute, Karaikudi 3, Madras, India). *Australian J. Chem.*, 14 (1961) 458–459.
The discrepancy between two expressions which have been derived for the phase-angle in alternating current polarography (Randles, *Discussions Faraday Soc.*, 1 (1947) 11 and Breyer *et.al.*, *Australian J. Chem.*, 8 (1955) 322) is discussed. It is concluded that the first of these is correct, the second being in error because of an inconsistency in the sign convention used in writing expressions for the current. [H.H.Ba.]

1009 – Catalytic ultramicro determination of thiocyanate on the basis of amperometric measurements (in Polish). E. Michalski and A. Wtorkowska (Department of Inorganic Chemistry, University, Łódź, Poland). *Chem. anal. (Warsaw)*, 6 (1961) 365–375.
Trace amounts of thiocyanate have been determined on the basis of its catalytic action on the iodine–azide reaction. The determinations were performed in the concentration range from 10^{-11}–10^{-8} g/ml, which corresponds to 10^{-10}–10^{-7} g of thiocyanate. The rate of reaction in given conditions is directly proportional to the concentration of the catalyst in solution. It was confirmed that the reaction is of the first order with respect to iodine, and its rate can be evaluated from the rate of iodine disappearance in the solution. The iodine concentration was measured amperometrically with a rotating platinum electrode, or with two indicator electrodes. The former procedure was found to be superior because of more accurate results. The deviation from the mean in this case is not greater than 10%, and in most cases is of the order of 3–4%. [Ad.Hu.]

1010 – Voltammetry of the H_2–$HClO_4$ system in acetonitrile on a platinised Pt-electrode: preparation of anhydrous $HClO_4$ solution in acetonitrile (in French). Jacques Vedel and Bernard Tremillon (Laboratoire de Chimie Analytique, École de Physique et de Chimie, Paris, France). *J. Electroanal. Chem.*, 1 (1959/1960) 241–247.
The system H_2/H^+ was studied electrochemically by determining current–electric tension curves at a platinised platinum electrode, in anhydrous acetonitrile. The oxidation of hydrogen dissolved in a perchlorate medium and the reduction of perchloric acid indicates that at this electrode the system is a fairly rapid one.
The coulometric preparation of a standard solution of perchloric acid in anhydrous acetonitrile, by oxidising hydrogen in perchlorate medium was investigated. [Author]

1011 – Oscillo-polarographic behaviour and determination of iodate and periodate (in German). A. Berka and J. Doležal (Department of Analytical Chemistry, Charles University, Prague, Czechoslovakia). *Anal. Chim. Acta*, 24 (1961) 476–480.
Because it was not possible to have good polarographic waves of iodate and periodate in an acid medium (1 *M* HCl, 1 *M* H_2SO_4, 1 *M* H_3PO_4, 1 *M* acetic acid, 1 *M* oxalic acid), the depolarisation of these two ions was studied in neutral, weakly basic and basic media. The determination of periodate in iodate may be carried out using iodate as a carrier electrolyte. The determination of iodate in periodate was performed in 5 *M* sodium hydroxide. [Ph. Me.]

1012 – Radiometric and amperometric titrations of copper with ^{3}H-anthranilic acid (in English). G. H. Aylward, J. L. Garnett, J. W. Hayes and S. W. Law (Radiation Laboratory, Departments of Analytical and Physical Chemistry, University of New South Wales, Sydney, Australia). *J. Inorg. & Nuclear Chem.*, 16 (1961) 350–355.
A method is presented as an illustration of a general technique for metal ion analysis. It consists of a radiometric titration in which metal ions are titrated with tritium-labelled organic reagents; the term "tritiometry" is proposed for this type of determination. In this paper titration of copper with tritium-labelled anthranilic acid is described. Amperometric titrations have also been carried out; radiometric and amperometric end-points are in good agreement.
A method of routine metal ion analysis is suggested in which an excess of tritiated organic reagent is added to the solution; the supernatant liquor is taken and counted after a suitable period. From this count, the original concentration of metal ion in the solution can be deduced. [Su.Mo.Ce.]

1013 – Polarographic determination of zinc, copper and lead in magnetite electrodes (in Polish). J. Gallus-Olender (Analytical Laboratory, Institute of Inorganic Chemistry, Gliwice, Poland). *Chemia anal.*, 6 (1961) 269–272.
A polarographic method of copper, lead and zinc determination has been developed to determine these metals in high-iron content materials. The concentration of determined metals was in the range 0.05–2%. Iron was reduced at pH 1.8 with hydroxylamine after fusing the sample with Na_2CO_3, dissolving in HCl, and evaporating with HNO_3 and HCl. The polarograms were obtained in solutions containing 0.01% gelatine. Copper was determined after additional acidification of

the solution with HCl. Results were calculated using the addition method. Depending on the concentration range the precision was 1–10%. [Ad.Hu.]

1014 – Temperature effects in alternating current polarography. H. H. Bauer and P. B. Goodwin (Faculty of Agriculture, University of Sydney, Australia). *Australian J. Chem.*, 14 (1961) 460–462.
The small amount of published data on the temperature coefficients of a.c. wave-heights is summarised. Results obtained with a number of inorganic depolarizers *e.g.* Cd(II), Tl(I), Sb(III), Cu(II), In(III), Pb(II), Sn(II) and Zn(II), demonstrate the efficacy with which temperature effects enable one to determine whether a process is diffusion-controlled or not. [H.H.Ba.]

1015 – Chemical properties in molten LiCl–KCl eutectic: metallic oxides (in French). Guy Delarue (Laboratoire de Chimie analytique, École de Physique et Chimie, Paris, France). *J. Electroanal. Chem.*, 1 (1959/1960) 285–300.
The solubility of certain metallic oxides in eutectic molten LiCl–KCl was studied. Intensity–electric tension curves were plotted to ascertain whether or not the oxides are dissociated in solution. The oxidising properties of Cu^{2+} and CrO_3 were used for classifying a certain number of redox systems. [Author]

1016 – The determination of water in plastic materials. V. W. Reid and L. Turner (Petrochemicals Ltd., Carrington Research Laboratory, Urmston, Manchester, Gt. Britain). *Analyst*, 86 (1961) 36–39.
The method is based on the Karl Fischer titration using a dead-stop end-point. Dry nitrogen is passed for 30 min through the granulated plastic which is maintained at 120° and thence to a titration assembly containing about 20 ml of reagent. An electric tension of 100 mV is applied between two Pt indicator electrodes and the current flowing is observed on a milliammeter. Before introducing the plastic into the gas stream the cell is adjusted to the dead-stop end-point by addition of reagent with the gas flowing until the nitrogen passes for 15 minutes without causing the dead-stop indicator to pass from the "dry" side back to the reference point. This procedure ensures that the gas train is completely dry. At this stage 20 g of polymer is introduced into the gas stream and the reagent is added in 0.1 ml portions to maintain the titration assembly on the "dry" side. The portion which maintains the titration assembly on the "dry" side for 15 min is taken as the end-point. [P.O.Ka.]

1017 – Polarographic catalytic waves of hydrogen and catalyst adsorption (in Russian). S. G. Mayranovskii (Institute of Electrochemistry, Academy of Sciences, U.S.S.R.). *Doklady Akad. Nauk S.S.S.R.*, 132 (1960) 1352–1355.
The influence of catalyst adsorption is shown by the example of the quinine-catalysed wave of hydrogen. Experimental data were obtained on a CLA type Polarograph at 25 ± 0.1°, with a mercury drop electrode with regulated drop-times. At $4 \cdot 10^{-4} M$ quinine concentration an inflexion is observed on the catalytic wave, which with increasing concentration turns into a peak. This doubling of the hydrogen wave is also observed on addition of surfactants to the solution, *e.g.* tetraethylammonium benzylsulphonate. [Ot.So.]

1018 – Polarographic determination of copper in Indian rubber-grade china clays (in English). A. S. Ghag, A. G. Dessi, K. V. Modac and M. B. Kabadi (Institute of Science, Bombay, India). *Science and Culture (India)*, 25 (1960) 686.
The authors have employed the polarographic technique to estimate copper in Indian rubber-grade china clays. 1 g of the clay was extracted with 14 g of NH_4OH (sp. gr. 0.88); the filtrate and washings were collected, about 15 g NH_4Cl and 10 ml 0.125% gelatine solution were added to these, and the solution made up to 250 ml. All the readings were taken on a Tinsley Polarograph. The standard was prepared by dissolving 0.25 g of electrolytic copper in a mixture of H_2SO_4 and HNO_3. All the clay samples investigated were found to contain only traces of copper. [R.S.Sa.]

1019 – The reduction wave of copper ion in potassium hydroxide supporting electrolyte (in English). Takeo Takahashi and Hideko Shirai (Institute of Industrial Science, University of Tokyo, Japan). *J. Electroanal. Chem.*, 1 (1959/1960) 408–415.
In d.c. polarograms of copper ions in potassium hydroxide solution the first, second and third reduction waves were observed according to the varying conditions of the concentrations of copper and potassium hydroxide, whilst in a.c. polarograms of copper ions, the second and third reduction waves were always found to be present.
According to the present study the first wave is considered to be due to the reduction of $Cu(OH)_2$ and the second and third waves to be due to the reduction of the $Cu(OH)_4^{2-}$ ion. [Authors]

1020 – Study of some supporting electrolytes for the simultaneous determination of Cu, Ni, Zn, and Co (in Spanish). F. Burriel-Marti, R. Gallego-Andreu and P. Perez-Carretero (Department of Analytical Chemistry, Council for Scientific Research, Madrid, Spain). *Anales real soc. españ. fis. y quim., (Madrid)*, 57B (1961) 253–258.
The following supporting electrolytes have been systematically studied: ammonium oxalate, lithium sulphate, sodium sulphate, sodium acetate, potassium thiocyanate and potassium thiocyanate + sodium acetate. It is proposed to determine first the copper using 0.5 *N* sodium acetate (+ 0.001% gelatin) and then the three other cations in the same medium, after addition of a drop of saturated potassium thiocyanate to 5 ml. [L.Gi.]

1021 – Polarographic analysis of gold and gold alloy plating solutions (in English). A. E. Knotowicz and G. Tatoian (The Patent Button Co., Waterbury, Conn., U.S.A.). *Plating*, 47(1960) 645–647.
The composition of a cyanide plating solution can be determined polarographically. The determination of Ag, Au, Cu, Ni and Zn is described.
Ag and Au are determined in 1 *N* KCN as supporting electrolyte, reading the diffusion current at —0.95 V for Ag, and between —0.95 and —1.7 V for Au. If Ni is present a correction must be made, because Ni gives a wave similar to that of Au.
Cu, Ni and Zn are determined in 1 *N* NH_3–1 *N* $(NH_4)_2SO_4$ as supporting electrolyte. 1 ml of conc. HNO_3 and 3 ml of conc. H_2SO_4 are added to the soln. and this is heated to fuming. After cooling, gelatin is added and the soln. diluted to 50 ml with the electrolyte. After the Au ppt. has settled, Cu is determined at —0.8 V, Ni between —0.8 and —1.275 V and Zn between —1.275 and —1.6 V. The value for Au must be corrected if Ag is present. Results are in agreement with chemical values within 1%, except for Zn, whose error is around 5%. [Gio.Ser.]

1022 – Electrolytic deposit of zinc ion on flowing mercury electrodes (in English). A. Rius, I. M. Tordesillas and A. Sacristan (Institute de Quimica-Fisaca Rocasolano, Madrid, Spain). *Electrochim. Acta*, 4 (1961) 62–71.
The reduction of the zinc ion at the mercury jet electrode has been studied in KCl and KNO_3 solution, with regard to the influence of temperature and the concentration of supporting electrolyte. It is concluded that the mechanism of the reduction varies according to the concentration of KCl. The results obtained with KNO_3 are similar to those obtained with dilute KCl. The processes become more and more reversible as the temperature is raised. [Authors]

1023 – The second and third waves of zinc found in a.c. polarography (in English). T. Takahashi and H. Shirai (Institute of Industrial Science, University of Tokyo, Japan). *J. Electroanal. Chem.*, 1 (1959/1960) 331–338.
In the a.c. polarography of zinc, the second wave, both in potassium salt and ammonium salt solutions, is presumed to be due to zinc hydroxide formed on the electrode surface in the presence of dissolved oxygen. But when alkali is added, the second wave in ammonium salt solution is found to be due to $Zn(OH)_2.(NH_3)_2$ at 0.01–0.05 *M* NH_3 and the third wave appears at pH > 7.3 in 2 *M* NH_3. While d.c. polarography gives only one wave, a.c. polarography shows two or three waves. [Authors]

1024 – Application of RADME to the chelatometric determination of metals employing the alternating current polarographic method (in English). M. Kodama (Department of Chemistry, Ibaraki University, Watari-machi, Mito, Japan). *Bull. Chem. Soc. Japan*, 34 (1961) 714–718.
Nitrilotriacetate (NTA) complexes of cadmium and lead show two polarographic steps, one due to direct reduction and the other to reduction of free metal ions formed by dissociation of the complexes. The later kinetic step makes estimation by amperometric titration of the metal ions by NTA impossible. A.c. polarograms, however, show only one wave, corresponding to the direct reduction of the complex: consequently, the a.c. polarographic analogue of amperometric titration could be used for the estimation. The procedure was successfully applied to the analysis of copper, cadmium and lead ions by titration with NTA, using the rapidly dropping mercury electrode (RADME). Surface-active substances (gelatin and camphor) had different effects at the DME and the RADME. [H.H.Ba.]

1025 – Polarographic studies of chloride complexes of cadmium in water solution, in methanol solution, and in water–methanol/or ethanol solutions (in Russian). Ya. I. Tur'yan and B. P. Zhantalaj (Lisicha Branch of the State Institute for Scientific Research and Design Applied to the Nitrogen Industry and to Organic Synthesis Products, State University of Kishinev, U.S.S.R.). *Zhur. Neorg. Khim.*, 5 (1960) 1748–1755.
The authors have studied the influence of the nature of solvents on the composition and the

stability of chloride complexes of cadmium. Polarographic determinations have been carried out at two constant values of the ionic strength in solutions of $LiNO_3$–LiCl.
(1) High ionic strength, $\mu = 2$, for values of Cl^- concentration varying from 0.0 up to 2.0 *M*, Cd^{2+} concentration $= 2 \cdot 10^{-4}$ *M*. The diffusion current and the half-wave values are reported in water–methanol solutions (methanol concentration in the range 0–100%) and in water–ethanol solution (ethanol concentration varying between 30 and 97.4%).
(2) Low ionic strength, $\mu = 0.01$, Cl^- concentration varying from 0.0 up to 0.01 *M*, and Cd^{2+} concentration $1 \cdot 10^{-4}$ *M*. The polarographic values are reported for the same water–alcohol mixtures, as quoted above.
The instability constants were determined by the conductometric, potentiometric and polarographic methods, at ionic strength values varying between 0.01 and 3.0, for the chloride complexes of cadmium in water solutions. The complexes observed in this solvent are $[CdCl]^+$, $[CdCl_2]$ and $[CdCl_3]^-$. With increasing ionic strength, the stoichiometric instability constants show a maximum corresponding with a maximum of the activity coefficient of cadmium ion. Stoichiometric and thermodynamic instability constants have been determined also for the complexes formed in water–alcohol solutions. They are $(CdCl_4)^{2-}$ and $(CdCl_5)^{3-}$ in addition to the complexes observed in water solutions.
A linear dependence is observed between the p*K* values and the lines of the inverse dielectric constant. The angular coefficient of these lines increases with increasing coordination number. From these angular coefficients an effective ionic radius has been derived for the Cd^{2+} ion, $r =$ 3.3 Å (mean value). [Li.Ne.Ro.]

1026 – Amperometric titration of cadmium with sodium selenite (in English). G. S. Deshmukh and O. P. Ashthana (Banares Hindu University, Varanasi, India). *J. Sci. Ind. Research (India)*, 20B (1961) 229.
Amperometric titration of cadmium acetate solution at an applied tension of —0.8 V *vs.* S.C.E. with sodium selenite has been carried out; an overall concentration of 60–80% alcohol and a pH of 6.8–7.2 was maintained during the titration. The results were very accurate and reproducible. [R.S.Sa.]

1027 – Polarographic method of simultaneous determination of indium and cadmium (in English). Teiichi Matsumae (Government Industrial Research Institute, Nagoya, Japan). *J. Electrochem. Soc. Japan, (Overseas Edn.)*, 27 (1959) E 240 – E 241.
The diffusion current of In and Cd has been studied in 1 *N* KI supporting electrolyte. At constant Cd concentration the diffusion current depends on the concentration of In and vice versa. SO_4^{2-} increases the diffusion current of In and shifts the half-wave electric tension to more negative values. In 0.1 *N* supporting electrolyte the effect is more marked. Cl^- has an effect similar to SO_4^{2-} but less intense; NO_3^- does not interfere and the Fe^{3+} influence can be eliminated by reducing it to Fe^{2+} with NH_2OH. Lead, which dissolves in KI forming PbI_4^{2-}, gives a reduction wave interfering with that of In. The method has been applied to zinc refinery products. The agreement with gravimetric results is good. [Gio.Ser.]

1028 – Polarographic determination of the equilibrium composition of Ti(IV) and Ti(III) ions in hydrochloric acid solutions and of ions participating in the process (in Russian). A. G. Stromberg and A. I. Kartushinskaya (Polytechnic Institute, Tomsk, U.S.S.R.). *Zhur. Fiz. Khim.*, 35 (1961) 1058–1063.
Based on the irreversible anodic-cathodic wave theory developed earlier by the authors, equations are derived for determining the composition of redox complexes participating directly in the electrode process, and for those predominant in the solution. The expressions have been applied in theoretical treatment of the experimental data obtained. It is shown that Ti(IV) and Ti(III) complexes which predominate in the solution have the composition $Ti(OH)_2Cl_2$ and Ti^{3+}, whereas those directly participating in the electrode process have the composition $TiOHCl^{2+}$ and $TiOHCl^+$. [Ot.So.]

1029 – Investigation of the thiocyanate complex using polarographic kinetic waves of titanium(IV) monothiocyanate (in French). S. Tribalat with the collaboration of D. Delafosse, C. Priolet and D. Zeller (Laboratoire de Chimie-Physique de la Faculté de Sciences de Paris, France). *J. Electroanal. Chem.*, 1 (1959/1960) 443–452.
Over a certain concentration range of thiocyanate ions, the values of the kinetic waves of the thiocyanate monocomplex with Ti(IV) are proportional to the concentration of these ions. When the waves are not disturbed by the presence of an acceptor of SCN ions, it is possible to study the reactions which result in the disappearance of these ions. Examples concerning the complex monothiocyanates of cobalt (III), iron(III) and chromium(III) are given. [Author]

1030 – Polarographic determination of germanium (in Russian). N. V. Staschkova and A. I. Selieanskaia (Akademi Nauk, S.S.S.R.). *Izvest. Sibirskoyo Otdel.*, (1959) 59–66.
According to the Ge content, a sample weighing 0.2–1 g is treated with a HNO_3–HF–H_3PO_4 mixture (or fused with Na_2O_2); in the first case excess acid is evaporated; in the second case, after water treatment, the hydrogen peroxide is eliminated by hydroxylamine salts and then acidified by means of H_2SO_4. The acid solution, measuring 15–30 ml, is transferred to a separating funnel, HCl (up to a final conc. of 9 *N*) is added and Ge is extracted twice with CCl_4 (40 + 20 ml); the organic layer is washed with 10 ml of 10 *N* HCl, Ge is transferred into water in two washings using 10 ml water at a time, the co-extracted As is oxidized with 3 drops 0.1 *N* I_2, an indicator is added (SIW-1 or phenolphthalein) together with 10 ml of buffer (0.1 *N* borate and 0.5 *N* acetate), the pH is corrected, if necessary, to 7–9 by means of 1 *N* NaOH. The solution is then brought to 50 ml (final Ge content less than 1.5 mg/50 ml), and polarographed under H_2 between —1.0 and 1.7 V.
If interfering ions (Te, Se, As and Cr) are absent, the metal can be dissolved in H_2SO_4 (1 : 3) and H_2O_2; after evaporation of the excess oxidant the pH is brought to 7–9 as above, the O_2 wave is suppressed by means of sulphite (if the conc. is above 0.04 *M*, add 0.001–0.002% gelatine in order to hinder the diffusion current), other interfering ions are complexed by means of Trilon B (which also improves the wave form) and polarography is started. Ge can be analyzed for contents of 0.1–0.01%. [Ca.Cas.]

1031 – Polarographic determination of germanium by means of extraction (in Polish). Z. Gregorovitz, D. Mazonska and D. Praisnar (Glivice Katedra Chim. Nieorg. Politechn., Slaskjei, Poland). *Hutnik*, 26 (1959) 407.
To the solution (Ge content 1–20 pg) conc. HCl is added (final conc. 9 *N*) and extraction by 2 × 40 ml CCl_4 is carried out; from the solvent, the Ge is transferred to 25 ml 2 *N* HCl which is in turn neutralised and, after addition of 10 ml 2 *M* Na_2CO_3, 5 ml 0.5 *M* complexon and 0.5 ml 0.05% gelatine is brought to 50 ml and polarographed from —12 V. The results are read against two calibration curves (ranges 0.0–5 pg and 0.0–25 pg). [Ca.Cas.]

1032 – The determination of tin in pure iron, mild steel and certain low-alloy steels by cathode ray polarography. P. H. Schloss (British Iron & Steel Research Association, Hoyle Street, Sheffield, Gt. Britain). *Analyst*, 86 (1961) 392–399.
The sample was dissolved in 20% HNO_3, carbonaceous matter oxidised with $KMnO_4$, excess of this reagent being destroyed with H_2O_2, and Sn coprecipitated as metastannic acid by MnO_2 added in the form of $KMnO_4$. The precipitate after thorough washing with hot water was dissolved in 1 : 1 HCl–water and 20 vol. H_2O_2. The solution was fumed with HNO_3 + 50% H_2SO_4 and oxidised with a few drops of sat. $KClO_3$ solution. This solution was finally made up in a base electrolyte containing 40% HCl (sp. gr. 1.18), 2% ascorbic acid and 10 mg peptone. Cathode ray polarograms with a Southern Analytical polarograph required a start electric tension of —0.1 V. If the sample contained W it was necessary to employ the derivative circuit and a start electric tension of —0.3 V. In the presence of 0.5% Mo a correction factor was necessary. Calibration curves were prepared by adding known amounts of Sn to solutions of pure Fe and treating as above. A range of 0.001 to 0.02% Sn was covered by this method. [P.O.Ka.]

1033 – The polarographic behavior of cerium(IV) and cerium(IV)–cerium(III) systems in sulphuric media. A direct determination of cerium (IV) (in English). Pier Giorgio Desideri (Institute of Analytical Chemistry, University of Florence, Italy). *J. Electroanal. Chem.*, 2 (1961) 39–45.
The Ce(IV) reduction in sulphuric media at bubbling smooth platinum electrodes was widely investigated. The influence on the ceric ion behaviour of H_2SO_4 ionic activity, the presence of catalysts, as well as temperature changes were observed. The conditions under which the redox Ce(IV)–Ce(III) system becomes reversible in sulphuric media are defined and the influence of acidity, catalysts and temperature are studied. Finally, a direct polarographic determination of Ce(IV) is described. [Author]

1034 – Determination of lead with potassium dichromate in technical alloys by amperometric detection of the equivalence point (in Spanish). F. Burriel-Marti and M.T. Garate (Central Laboratory of R.E.N.F.E.). *Anales real soc. españ. fis. y quim.*, 57B (1961) 229–230.
After dissolving the alloy with a mixture of diluted nitric and hydrofluoric acids, the amperometric titration is performed with $K_2Cr_2O_7$, at a pH adjusted between the limits 1.8–2.5. A platinum indicator electrode and a calomel electrode are used, without any need for external polarisation. [L.Gi.]

1035 – An ion exchange separation and polarographic determination of small amounts of

lead and zinc in the presence of cobalt. R. Carson (Rhoanglo Mine Services Ltd. Research & Development Division, Kitwe, Northern Rhodesia, South Africa). *Analyst*, 86 (1961) 198–200.
The column is prepared from 50–100 mesh De-acidite FF poured in a slurry in 1% v/v HCl into a 100 ml burette with a glass wool plug. The column contains *ca.* 33 ml. Wash with 300 ml of a solution containing 1% v/v HCl and 1% v/v sat. SO_2 solution, 1 l of H_2O and then 300 ml of 2 *N* HCl. The sample, containing 1 g of either Co, Cu, Fe, Ni or Mn and 0.1 mg each of Pb and Zn in 50 ml of 2 *N* HCl, was added to the column and eluted with 2 *N* HCl until the effluent was nearly colourless. Last traces of major constituents were eluted with 4 × 50 ml of 0.5 *N* HCl. The Pb and Zn were then eluted with 100 ml of 0.005 *N* HCl. This eluant was evaporated to dryness, dissolved in a solution containing 250 g NaCl and 50 ml 2 *N* HCl per liter, buffered with 5 ml of 38.5% w/v ammonium acetate–28.6% v/v acetic acid and polarographed after adding 0.5 ml of 1% gelatine as maximum suppressor. Recoveries were *ca.* 95% for Pb and *ca.* 90% for Zn. [P.O.Ka.]

1036 – The analysis of lead tannate and related chelates by an amperometric method. S. E. Drewes (Paint Industries Research Institute, University of Natal, Durban, South Africa). *Analyst*, 86 (1961) 104–106.
This ingenious method inverted the usual amperometric method in that the release of Pb^{2+} into solution from an insoluble complex was followed amperometrically by titration with dilute HNO_3. 0.2–0.3 g of the complex was suspended in 25 ml of 20% v/v aqueous ethanol and after removing O_2 with N_2 this suspension was amperometrically titrated against 0.2 *N* HNO_3 using a dropping mercury electrode at an electric tension of —1.0 or —1.2 V *vs.* S.C.E. Plotting the current (corrected for dilution by the added HNO_3) against the volume of HNO_3 gave an inverted L- shaped curve whose point of intersection corresponded to the end-point. In three typical determinations the method gave results within 3% of those given by gravimetry. [P.O.Ka.]

1037 – Amperometric determination of phosphorus in food (in Polish). E. Szyszko (Department of Food Research, State Department of Hygiene, Warsaw, Poland). *Roczniki Państwowego Zakladu Hig.*, 12 (1961) 267–277.
A rapid and accurate method of phosphorus determination has been worked out which is based on amperometric titration of phosphate ions with standard lead acetate solution. The food sample was ashed, treated with nitric acid, evaporated to dryness and the residue dissolved in 50% acetic acid. 1 ml of 1% tylose solution was added, the pH was adjusted to 6 with 10% NaOH, and the sample was diluted to 100 ml. After deaeration the diffusion current on a mercury drop electrode was recorded at —1.0 V *vs.* S.C.E. The equivalence point was found from the graph. Only Ca can interfere if present in a ratio greater than Ca : P = 1 : 2. The variation coefficient equals 0.4% when 50 mg P in 100 gm sample was determined. [Ad.Hu.]

1038 – Catalytic microdetermination of phosphate by means of amperometry (in Polish). E. Michalski and L. Walewski (Department of Inorganic Chemistry, University of Lódź, Poland). *Chemia anal.*, 6 (1961) 273.
Phosphate was used as a catalyst for the molybdate reduction by means of iodide. The course of the reaction was observed amperometrically by measuring the iodine concentration. On this basis phosphate could be determined in the order of 10^{-7} g/ml with satisfactory precision. [Ad.Hu.]

1039 – Amperometric determination of quadrivalent and tervalent vanadium when present together (in Russian). I. A. Tserkovnitsa and N. A. Kustova. *Vestn. Leningrad Univ., Ser. Fiz. i. Khim.*, 16 (1960) 148–149.
At a pH of 3–4, vanadium salts complex with EDTA forming a stable complex which permits a good determination of V^{3+} and V^{4+}. Using a vibrating Pt electrode at + 0.9 V *vs.* S.C.E. and 0.1 *N* EDTA as titrant, a curve can be obtained with two inflexions corresponding to V^{3+} and V^{4+} respectively. [Gio.Ser.]

1040 – Polarographic behaviour of vanadium and iron in thiocyanate (in English). G. S. Deshmukh and J. P. Srivastava (Chemical Laboratories, Banares Hindu University, Varanasi 5, India). *Bull. Chem. Soc. Japan*, 34 (1961) 325–328.
The polarographic behaviour of vanadium and iron in solutions containing thiocyanate has been studied. The effects of pH and of depolarizer and supporting electrolyte concentration were reported. Vanadium(IV) was reduced in two reversible, one-electron stages, iron(III) in a single one-electron step. The calibration curves were linear. The presence of molybdenum(VI), tungsten (VI) and copper(II) ions interfered with the estimation of vanadium, but cobalt, manganese, nickel, chromium(III), ammonium, nitrate, chloride and bisulphate did not; of these ions, only tungsten and molybdenum interfered with estimation of iron. A recommended procedure for the simultaneous determination of iron and vanadium is given in detail. [H.H.Ba.]

1041 – The polarography of arsonic acids. C. P. Wallis (Department of Biochemistry, University of Edinburgh, Scotland). *J. Electroanal. Chem.*, 1 (1959/1960) 307–313.
The polarograms of certain *ortho*-substituted arsonic acids show unusual features, which are attributed to adsorption on the basis of the corresponding electrocapillary curves. It is concluded that the adsorption of these compounds alters their reducibility and at the same time decreases the diffusion current; the three types of effect to be expected are illustrated by the arsonic acids investigated. Although desorption was observed the effect on the polarogram was minor.
[Author]

1042 – Polarographic determination of antimony in refined lead (in English). V. T. Athavale, R. G. Dhaneshwann, M. M. Nehta and M. Sundaresam P. Antal (Analytical Division, Atomic Energy Establishment, Trobay, Bombay, India). *Analyst*, 86 (1961) 399–401.
A 1 g sample was dissolved in 5 ml 20% HNO_3, 1 ml conc. H_2SO_4 was added and the solution diluted to 25 ml with water. A 10 ml aliquot was evaporated to fuming, 3 ml of *N* H_2SO_4 added and the solution polarographed. The half-wave electric tension of Sb was —0.32 V *vs.* S.C.E. The limit of sensitivity was 10 p.p.m. and accuracy ± 5%. There was no interference from Cu, Fe, or Bi when present in amounts equal to Sb. Sn if present to a greater extent than Sb causes analysis figures for Sb to be depressed (72% recovery of Sb for Sn : Sb = 2 : 1). [P.O.Ka.]

1043 – Electrochemical oxidation of HO^- and O^{2-} ions in LiCl–KCl molten eutectic (in French). Guy Delarue (Laboratoire de Chimie Analytique, École de Physique et de Chimie, Paris, France). *J. Electroanal. Chem.*, 1 (1959/1960) 13–25.
Current–electric tension curves of solutions of potassium hydroxide in molten LiCl–KCl eutectic exhibit an oxidation wave that can be attributed to HO^- or to O^{2-} ions. It can, in fact, be assumed that HO^- ions do not exist in the melt, but are spontaneously converted to O^{2-}ions.
From investigations of solutions of some metal oxides (PbO, NiO, CaO, MgO, CuO) it can be inferred that in the molten eutectic these oxides are dissociated; these solutions contain O^{2-} particles, which can be oxidized, either chemically or electrochemically. [Author]

1044 – Rapid polarographic determination of tin in ferrotungsten, metallic tungsten and tungsten ores (in Czech.). S. Král and V. Rett (Sonp, Kladno, Czechoslovakia). *Hutnické listy*, 15 (1960) 638–639.
For determinations using ferrotungsten and metallotungsten, 2 g are dissolved in a platinum dish with 20 ml HNO_3 (1 : 1) and the required amount of HF. 10 ml H_2SO_4 (1 : 1) are added and the mixture is heated until fuming. After cooling, the mixture is transferred to a 100 ml flask and 10 ml conc. HCl and 2 g reduced or metallic iron are added. After heating for 10 min at 60°, Fe^{3+} is reduced to Fe^{2+}, WO_3 to W_2O_5, and Sn^{4+} to Sn^{2+}. 20 ml HCl and 2 g iron are again added and the reduction is completed with 1 g hydrazine sulphate. After cooling, 10 ml gelatin (0.5%) are added, the mixture is diluted to 100 ml and filtered to remove W_2O_5. The polarogram of the filtrate is registered. The procedure can be completed in 4 h.
For tungsten ore concentrates, 2 g are powdered and fused with 5 g of Na_2O_2 in an iron crucible. The mass is taken up with water, diluted to 200 ml and filtered. The filtrate is acidified with HCl, evaporated to 50 ml, transferred to a 100 ml flask and treated as above. [Gio.Ser.]

1045 – Errors in the polarographic determination of uranium in microquantities after concentration from waters and solids (in German). P. Antal (Analytical Institute of the University, Vienna, Austria). *Mikrochim. Acta*, 2 (1961) 235–244.
The catalytic nitrate wave is used for the determination. Concentrations lay between 10^{-5} and 10^{-8} *M*. The form of the polarographic curve reveals the presence of disturbing substances which appear to be W, Mo, Pt, V and Sn. When these elements are present it is better to use the fluorimetric method. [H.L.Ki.]

1046 – Analytical application of the hanging mercury drop electrode. IV. Analysis of traces of impurities in uranium salts (in English). W. Kemula, E. Rakowska and Z. Kublik (Institute of Physical Chemistry, Polish Academy of Science, and Department of Inorganic Chemistry, Warsaw University, Poland). *J. Electroanal. Chem.*, 1 (1959/1960) 205–217.
Conditions have been evaluated for the rapid determination of Cu, Pb and Cd in U compounds; 10^{-6}% Cd and 10^{-5}% Cu and Pb can be determined by the method proposed.
The analysis time, dependent on the compound being analysed, is *ca.* 1–2 h. The precision is about ± 10%. The determination is performed in carbonate solution in which the $UO_2(CO_3)_3^{4-}$ complex is reduced at —1.0 V, which does not influence the reduction of ions with more positive reduction electric tensions.
An investigation was made on the concentration range in which it was supposed that Cu, Pb and Cd carbonates would precipitate and interfere with the determination. This type of interference

was observed when the concentration of Cu exceeded 10^{-6} *M*, and that of Cd and Pb exceeded 10^{-5} *M*, *i.e.* at higher concentrations than those we wished to determine. It was found that Cu carbonate causes greater disturbances of current than Pb and Cd carbonates. In the case of the Cu oxidation current a few minima were observed. During the reduction of Cu carbonate suspension a few cathodic minima were also noted. [Authors]

1047 – A polarographic study of a sulphuric solution of hexavalent uranium (in Russian). E. A. Kanevskij and G. R. Pavlovskaya. *Zhur. Neorg. Khim.*, 5 (1960) 1738–1742.
A 0.0007 *M* UO_2SO_4 solution in H_2SO_4 of concentration varying from 0.02 to 4.0 *N* gives three polarographic waves corresponding to the U(VI) → U(V), U(V) → U(IV) and U(IV) → U(III) reductions. In the lower range of acid concentrations (0.02–1.0 *N*) it is shown that, as the first diffusion current increases, a corresponding decrease of the second wave causes their sum to remain approximately constant at 8.35–8.72 μA.
The decrease of the third reduction wave is not explained by the increase of the viscosity of the solution, which, on the contrary, can account for the decrease of the first reduction wave from 7.92 to 7.39 μA, as the acid concentration varies from 2–4 *N*.
The half-wave values of the three reduction waves are reported for 0.0007 and 0.0061 *M* UO_2SO_4 in 0.02–4 *N* sulphuric acid. The half-wave of the second wave (U(V) → U(IV)) is linearly dependent on the mean activity of the sulphuric acid. [Li.Ne.Ro.]

1048 – Influence of anions on the reduction of uranyl ions on a dropping mercury electrode (in Russian). A. I. Alekperov and S. I. Zhdanov. *Zhur. Neorg. Khim.*, 5 (1960) 1743–1747.
The authors report a study on the influence of chloride, nitrate, sulphate, oxalate and fluoride ions on the half-wave of uranyl ion.
Chloride and nitrate ions do not exhibit any evident influence on the reduction wave of the uranyl ion; on the contrary, the other ions cause a shift of the half-wave value toward more negative values in weakly acid solutions, and a strong increase of the wave in strongly acid ones. The shift is a consequence of the formation of a complex of uranyl ion with the anions, but the increase of the diffusion current reveals an accelerated disproportionation of the uranyl ions. These anions form stable complexes with U(IV), thus increasing the disproportionation of uranyl. [Li.Ne.Ro.]

1049 – A.c. polarographic investigation of dismutation. B. Breyer, J. R. Beevers and H. H. Bauer (Section of Agricultural Chemistry, Dept. of Agriculture, University of Sydney, Australia). *J. Electroanal. Chem.*, 2 (1961) 60–65.
The dismutation reaction of the U(V) ion has been studied by a.c. polarography; various supporting electrolytes at different acid concentrations were used. An initial increase in the height of both a.c. waves may be due to the suppression of hydrolysis of the electroactive species. The first wave decreases at higher acid concentrations due to dismutation; relative values for the equilibrium constant of the dismutation process in different electrolytes have been calculated, and are in agreement with values reported from d.c. polarographic studies. The decrease in height of the second a.c. wave at high acid concentrations seems due to a change in the structure of the electrical double-layer. [Authors]

1050 – The determination of uranium in sea water by pulse polarography. G. W. C. Milner, J. D. Wilson, G. A. Barnett and A. A. Smales (Chemistry Division, Atomic Energy Research Establishment, Harwell, Berks., Great Britain). *J. Electroanal. Chem.*, 2 (1961) 25–38.
A procedure is described for the determination of the uranium content of sea water. The uranium is first separated and concentrated from 4 l of sea water by solvent extraction with di-(2-ethylhexyl)-phosphoric acid in carbon tetrachloride. A further purification of the uranium is carried out by the extraction of uranyl nitrate into ethyl acetate, and the uranium concentration is found by pulse polarography using the peak from a perchloric acid–tartrate supporting electrolyte. Uranium-237 is employed as a radioactive tracer to measure the percentage recovery of uranium per litre. [Authors]

1051 – Estimation of uranium in ores by a.c. polarography. B. Breyer (Section of Agricultural Chemistry, Department of Agriculture, University of Sydney, Australia). *J. Electroanal. Chem.*, 1 (1959/1960) 345–350.
Uranium can be conveniently estimated by a.c. polarography. The a.c. method permits successful uranium analysis in the presence of a number of ionic species, particularly vanadate ion, which seriously interferes in conventional polarography.
Examples illustrating the use of the method for the analysis of uranium ores are given. [Author]

1052 – Investigation of the kinetics of the electroreduction of iron on the mercury drop

electrode (in Russian). V. F. Ivanov and Z. A. Yofa (M. V. Lomonosov State University, Moscow, U.S.S.R.). *Doklady Akad. Nauk S.S.S.R.*, 137 (1961) 1149–1152.
The degree of irreversibility of the reduction of divalent iron ions on the mercury drop electrode has been investigated, as well as the influence of iron and hydrogen ion concentration, and of the kind and concentration of the supporting electrolyte on the kinetics of the process. A visual polarograph was used for measuring the electric tension of the Hg drop electrode by the compensation method. A 1 *N* calomel electrode was used for comparison. In the electrolytic vessel hydrogen and glass electrodes were included making it possible to measure pH to ± 0.05 units at any time. The temperature was $25 \pm 0.1°$. Investigation of the limiting current I_d dependence on ferrous ion concentration in the range $10^{-4} - 10^{-2}$ *N* has shown that at a pH less that 4.5, I_d agrees with the Ilkovic equation, at n = 2, and a diffusion coefficient of $0.76 \cdot 10^{-5}$ cm²/sec. The mechanism of the electrode reaction is further described in detail. [Ot.So.]

1053 – An evaluation of the formate method for simultaneous polarographic determination of copper and lead in steel. P. H. Scholes (British Iron & Steel Research Association, Hoyle Street, Sheffield, Gt. Britain). *Analyst*, 86 (1961) 116–124.
This paper describes a modification of Curry's method for determining Cu and Pb in steel and defines the precise application of the modified method for Cu in steels containing up to 2% Mo. Since Sn, As, Ti and Mo are reduced at the same electric tension as Pb, these elements must not be present in greater than trace quantities. At 0.1%, Cu can be determined with a standard deviation of 0.006% if Mo< 0.2% and the precision is decreased when Mo is in the range 0.2–2%. At 0.05% Pb the standard deviation is 0.008%. Dissolve 1 g sample in 12 ml of warm HCl (1 : 1), oxidise the carbides with a sat. solution of $KClO_3$ added dropwise followed by concentration to 6–7 ml on a hot-plate. Add 5 ml of 20% w/v $N_2H_4 \cdot HCl$, 5 ml sat. HCOONa and 2 ml 0.5% starch solution. Heat at 90° until Fe^{3+} is completely reduced, cool, dilute to 20 ml. Deoxygenate with N_2 and polarograph on a C.R. polarograph using a start electric tension of —0.05 V for Cu and —0.34 V for Pb. At lower concentrations of Cu, a larger quantity (up to 5 g) of sample is dissolved in aqua regia and most of the iron is removed by extraction with *iso*butyl acetate before reduction with N_2H_4. [P.O.Ka.]

1054 – Polarographic investigation of the compounds obtained with O_2 in aqueous Co(II)-2,2′-dipyridyl solutions (in Italian). S. Cabani (Institute of Physical Chemistry, University of Pisa, Italy). *Gazz. chim. ital.*, 90 (1960) 1410–1427.
By bubbling O_2 into a Co(II)-dipyridyl neutral solution, a brown "oxygen carrier" compound is obtained, which is irreversibly transformed by ageing into the red Co(III) complex. The system $[Co(dipyr)_3]^{2+}$–$[Co(dipyr)_3]^{3+}$ is polarographically reversible ($E_{1/2} = +0.08$ V/S.C.E.) while the oxygen carrier yields a cathodic step at —0.1 V/S.C.E. A reliable interpretation of the electrode reaction is given. [Fr.Pan.]

1055 – Polarographic study of metal ion complexes with globin. II. Cobalt, nickel, zinc and cadmium at pH 5.0 and 6.6 (in English). G. H. Ahuja and C. S. Narwani (D. and H. National College, Bombay, India). *J. Indian Chem. Soc.*, 37 (1960) 741.
Polarograms of Co, Ni, Zn and Cd at various concentrations (0.0075–0.02 *M*) in the presence of globin at pH 5.0 and at 37° show that the diffusion currents in the presence of 1.0% globin are less than those in 0.01% indicating that the metal ion forms complexes with globin, the *c*-COOH groups of which ionise between pH 2.0 and 5.5. In the presence of 1.0% globin, the diffusion current decreases with time and is constant after 75 min in the case of Co, Ni and Zn and 60 min in the case of Cd. The number of g atoms of each metal combined with one g mol of globin has been calculated. The maximum number of metal atoms combined with one molecule of globin is found to be 24 in the case of Zn; 20 atoms of the bivalent metal are accounted for by 40 COOH groups and 4 and 8 SH groups present in one molecule of globin. Lower values at different concentrations of other metals may be attributed to the ionisation of protein-bound metal.
At pH 6.6, the number of g atoms of Co, Ni, Zn and Cd combined with one g mol of globin has been found to be 18–20. Since the imidazole-x group ionises between pH 6 and 8, it is presumed that there is a maximum of 40 histidine residues in one molecule of globin. [R.S.Sa.]

1056 – Polarographic determination of the formation constant of nickel(II) sulphate complex (in English). N. Tanaka and H. Ogino (Department of Chemistry, Faculty of Science, Tohoku University, Senclai, Japan). *Bull. Chem. Soc. Japan*, 34 (1961) 1041–1045.
Auxiliary complexing agents were used to determine the formation constant of nickel(II) sulphate (*cf.* Tanaka and Kato, *ibid.*, 32 (1959) 516).
K_{NiSO_4} at ionic strength 0.2 was found to be 14.3 ± 0.4 at 15°, 11.6 ± 0.9 at 25° and 14.6 ± 0.7 at 35°. [H.H.Ba.]

1057 – Polarographic study of the reaction between nitrosyl–ruthenium complexes and hydrazine. E. N. Jenkins (U.K.A.E.A. Research Group, Atomic Energy Research Establishment, Harwell, Berks., Gt. Britain). *Nuclear Sci. Abstr.*, 15 (1961) 766, *Abstr. No.* 5927.

1058 – A polarographic and spectrophotometric investigation of rhodium(III) bromo-complexes (in English). Danilo Cozzi and Francesco Pantani (Institute of Analytical Chemistry, University of Pisa and Florence, Italy). *J. Electroanal. Chem.*, 2 (1961) 72–79.
In bromide solutions and in the presence of 0.03% gelatin, Rh^{3+} yields well-developed polarographic waves. The process is a practically reversible three-electron reduction. Several bromo-complexes appear to be in solution at the same time, when the pH is lower than 3. Two maxima are observed in the absorption spectrum. Stability constants of the complexed forms were computed and resolution of the spectra was achieved. The results were confirmed by electrophoresis and anion-exchange resins. [Authors]

1059 – Influence of monovalent alcohols on polarographic maxima of the first kind (in German). K. Schwabe and U. Mai (Institute for Electrochemical and Physical Chemistry, Technical College, Dresden, Germany). *J. Electroanal. Chem.*, 1 (1959/1960) 54–60.
The suppression of the O_2, Hg_2^{2+} and Ni^{2+} maxima by methanol, ethanol, *iso*propanol, *n*-propanol, *iso*butanol and *n*-butanol, was measured in relation to the alcohol concentration and compared with the viscosity, the interfacial Hg–solution tension and the surface tension of the solutions. No connection was found between the relative suppression and the viscosity, or the interfacial tension but the relative suppression increased strongly with decreasing surface tension. The results indicate that the adsorption of the alcohols at the surface of the Hg drop increases with increasing alcohol concentration and increasing chain length. [Authors]

1060 – Polarographic and spectrophotometric studies on trimethyl pyruvic acid (in English). M. Takagi (College of Agriculture, University of Osaka Prefecture, Sakai, Japan). *Bull. Chem. Soc. Japan*, 34 (1961) 905–910.
The variation of the limiting polarographic current of trimethylpyruvic acid is discussed in terms of the dissociation and hydration of the depolarizer. The dissociation constant was determined spectrophotometrically ($pK_a = 1.52$ at 25°), hydration constants from kinetic measurements ($K_h = [AH_{aq}]/[AH] = 0.46$ at 25°; for the trimethylpyruvate ion, rate constant of dehydration was $2.8 \cdot 10^{-2}$ sec^{-1} at pH 5 and 25°). An equation derived to predict the variation of limiting current with pH was in excellent agreement with experimental results at pH values greater than 0.5, but differed appreciably at lower pH values. Rate constants for dissociation and recombination of trimethylpyruvic acid were found to be respectively $6.0 \cdot 10^5$ sec^{-1} and $1.4 \cdot 10^7$ l mol^{-1} sec^{-1}. [H.H.Ba.]

1061 – On the polarographic reducibility of amidoximes. II. Reducibility of aliphatic amidoximes (in German). J. Mollin and F. Kašpárek (Chemical Institute, Palacky University, Olomouc, Czechoslovakia). *Collection Czechoslov. Chem. Communs.*, 26 (1961) 2438–2440.
0.001 *M* solutions in 50% ethanol were prepared of the individual amidoximes. 2 ml of these solutions were mixed in a vessel according to Kalousek with 2 ml of Britton-Robinson buffer, and after removal of oxygen, polarograms were registered. Results are tabulated giving values of $E_{1/2}$, $dE_{1/2}/dpH$ and the pH range of reducibility. Acetamidoxime is reduced only in an acid range, and probably only the protonised form can be reduced. Trichloroacetamidoxime behaves similarly giving a two-electron diffusion-controlled wave, accompanied by two more negative ones probably corresponding to the reduction of the two chlorine atoms in the molecule. [Ot.So.]

1062 – Amperometric argentimetric and mercurimetric titration of sulphydryl. I. Argentimetric titration. I. M. Kolthoff and J. Eisenstadter (School of Chemistry, University of Minnesota, Minneapolis, Minn., U.S.A.). *Anal. Chim. Acta*, 24 (1961) 83–90.
Amperometric argentimetric titrations of the sulphydryl of cysteine, glutathione, thioglycollic acid and 2-mercaptoethanol with a rotating platinum wire electrode (R.Pt.W.E.) were carried out in ammonia buffers. For glutathione and 2-mercaptoethanol the end point is found at the stoichiometric ratio. Cysteine yields high results, the titration being performed in a buffer of pH 9.05 (ammonia) or in 0.133 *M* tris buffer (tris-hydroxymethylaminoethane and its salt), acidified with nitric acid to pH 7.4. The error is of the order of 50%. With thioglycollic acid the positive error is about one half of that found with cysteine, but this error can be eliminated when working in the presence of sulfite. For cysteine, the error is reduced in the presence of 0.1 *M* sulfite and it becomes equal to zero at cysteine concentrations $\leqslant 5 \cdot 10^{-5}$ *M*. [P.Me.]

1063 – Amperometric argentimetric and mercurimetric titration of sulphydryl. II. Mercurimetric titration. I. M. Kolthoff and J. Eisenstadter (School of Chemistry, University of Minnesota, Minneapolis, Minn., U.S.A.). *Anal. Chim. Acta*, 24 (1961) 280–293.

The amperometric mercurimetric titration of cysteine(RSH), glutathione(GSH), thioglycollic acid(TSH) and 2-mercaptoethanol(ESH) at a rotating mercury pool electrode(RMPE) has been studied. At pH 9, a sharply defined end-point corresponding to the composition$(XS)_2Hg$ is obtained. With a rotating platinum wire electrode (RPtWE) and under the same conditions, the titration of RSH and GSH gives two breaks, corresponding to compositions $(RS)_2Hg$ and $(RS)_2Hg_2$ respectively. With the same electrode, TSH and ESH give only one clear break corresponding to $(TS)_2Hg$ or $(ES)_2Hg$. The RMPE can also be used for the accurate mercurimetric titration of the thiol compounds at pH 2 in the presence of 0.01 *M* sulfur dioxide. [P.Me.]

1064 – Investigation of the adsorption wave of glutathione (in Polish). Z. Bežyk (Department of Food Investigation, Academy of Medicine, Warsaw, Poland). *Acta Polon. Pharm.*, 18 (1961) 25–38.

The influence of thymol on the adsorption waves of glutathione was investigated as a function of pH and concentration of the solution. Within the pH range 2–7, the hydrogen ion concentration has no significant effect on the adsorption wave. At concentrations of about $2 \cdot 10^{-3}$ *M*, thymol can remove the adsorption waves of glutathione in Britten–Robinson and acetate buffers. Small amounts of thymol eliminate the cathodic wave of oxidized glutathione. After elimination of the adsorption wave, the half-wave electric tension of glutathione is shifted under the influence of thymol to more negative values. The direction of this type of change on anodic waves is opposite to changes on cathodic waves. [Ad.Hu.]

1065 – Studies on the catalytic double wave of cysteine by oscillographic polarography (in English). M. Shinagawa, H. Imai and H. Nezu (Laboratory of Analytical Chemistry, Faculty of Science and Minami College, Hiroshima University, Japan). *Bull. Chem. Soc. Japan*, 34 (1961) 445–449.

Oscillographic polarography as introduced by Sevcik (*Collect. Czechoslov. Chem. Communs.*, 13 (1948) 349) was used to study systems containing cobalt(II), cysteine, gelatine and methyl cellulose, a mixture intended as a tentative model for the catalytic protein wave. It is suggested that all the substances are adsorbed at electric tensions less negative than —1.6 V *vs.* S.C.E., and the catalytic wave appears at these tensions; at tensions more negative than —1.63 V, the cobalt(II)–cysteine complex is desorbed and the current decreases, since the complex catalyses the reduction of the hydrogen ions. At tensions more negative than —1.7 V, methyl cellulose is desorbed, and the current again increases since more surface is now available for the reduction process; this is the second wave. [H.H.Ba.]

1066 – Polarographic determination of thiourea (in Czech). V. Medonos and M. Vávrová (Institute of Chemical Technology, Prague, Czechoslovakia). *Chem. Průmysl*, 10 (1960) 234–237.

In *N* H_2SO_4, thiourea gives a polarographic wave at the d.m.e. The limiting current between —0.2 to —0.5 V *vs.* S.C.E. is proportional to the thiourea concentration in the range $2–6 \cdot 10^{-3}$ *N*. Cd acetate is used to precipitate sulphides. Cyanamide, dicyanamide and urea do not interfere. Using a 0.1 *N* Hg_2SO_4 electrode as a comparison electrode, no external voltage is necessary. A calibration curve is used for the calculation and the average error is $\pm$ 2%. The method is particularly suitable for determinations in calcium cyanamide. [Gio.Ser.]

1067 – Polarographic determination of divinylbenzene in products of diethylbenzene dehydrogenation (in Polish). J. Pašciak (Research Laboratory, Chemical Works, Oświecim, Poland). *Chemia anal.*, 6 (1961) 99–110.

On the basis of chromatographic separation on an Al_2O_3 column and literature data, polarographic properties of *p*- and *m*-divinylbenzene (DVB), and ethylvinylbenzene (EVB) were investigated. It was found that DVB isomers are reduced at the dropping electrode in two steps, while EVB isomers were reduced in one step. Using 0.1 *M* $(C_4H_9)_4NI$ in dimethylformamide the following half-wave values of the electric tension were given (*vs.* S.C.E.): *p*-DVB —2.15 V, —2.48 V; *m*-DVB —2.26 V, —2.43 V; mixture of EVB —2.45 V. In the presence of methanol, ethanol, phenol or other proton donors, the polarographic waves were sufficiently separated. On this basis it was found possible to develop a method for the quantitative determination of the products of diethylbenzene dehydrogenation. The limiting current depends linearly upon the DVB concentration in the mixture with EVB. The presence of styrene and naphthalene has no influence on the DVB determination. The method developed was controlled using technical samples. It was found that this method is superior to others. A single determination takes about 15–20 min. [Ad.Hu.]

1068 – Simultaneous polarographic determination of a system of *o*-nitroanisole, *o*-chloronitrobenzene and *o*-nitrophenol (in English). K. Honda and S. Kikuchi (Institute of Industrial Science, University of Tokyo, Chiba, Japan). *Bull. Chem. Soc. Japan*, 34 (1961) 529–532.

Simultaneous estimation of *o*-nitroanisole, *o*-chloronitrobenzene and *o*-nitrophenol was possible in 20% methanol solution containing 0.8 *M* sodium hydroxide. Though the solution was unbuffered, variation of the concentration of one of the components did not appreciably affect the wave-heights or positions of the steps of the other components. *o*-Nitrophenol was directly measured, from the height of its step, with an accuracy ± 10%. Over-compensation for the residual current facilitated the estimation of the other components, which were determinable with an accuracy of 10–20%. [H.H.Ba.]

1069 – Amperometric titration of some organic reducing reagents with potassium dichromate (in Russian). N. S. Sukhobokova. *Vestnik Leningrad Univ. Ser. Fiz. i Khim.*, 16 (1960) 149–150.
Quinol, *p*-methylaminophenol, *p*-aminophenol and *p*-phenylenediamine are determined by titration with 0.2 *N* $K_2Cr_2O_7$ using 0.5–2 *N* H_2SO_4 as supporting electrolyte. A platinum-wire microelectrode or a platinum disk electrode rotating at 800 r.p.m. are used at +1 V *vs.* S.C.E. The error in the determination of concentration is < 6% and the titration curves are reproducible. [Gio.Ser.]

1070 – Voltammetric determination of antioxidants at a wax-impregnated graphite electrode. E. Barendrecht. (Central Laboratory of the Netherlands State Mines, Geleen, The Netherlands). *Anal. Chim. Acta*, 24 (1961) 498–499.
The oxidation electric tensions of antioxidants of both the phenolic and the amino type are shifted in the same sense (*i.e.*, more negative at higher pH values), since hydrogen ions are always involved in the anodic oxidation process. Therefore, a supporting electrolyte of high pH can be used, with the result that the wave-form is considerably improved. With a rotating electrode having a speed of *ca.* 500 rev/min concentrations down to $5 \cdot 10^{-7}$ *M* can be detected. [P.Me.]

1071 – On quantitative estimation of the influence produced by substituents on the polarographic reduction of some methyleneimine compounds (in Russian). Yu. P. Kitaev, G. K. Budnikov and others (Chemical Institute, Kazan Branch, Academy of Sciences, U.S.S.R.). *Doklady Akad. Nauk S.S.S.R.*, 137 (1961) 862–865.
Hammett's equation was applied to data on the polarographic reduction of phenylhydrazones, thio- and semithiocarbazones of some aromatic aldehydes—benzoic, cuminic, dimethylaminobenzoic, *m*-nitrobenzoic aldehyde and also acetophenone and chloroacetophenone. The polarographic investigation was carried out using 10^{-4} *M* solutions in 20% methanol–aqueous solutions, with phosphate–borate buffer, pH 6.0, as supporting electrolyte. Results, including the number of electrons taking part in the reduction, slope of the straight line $E = f(\log i/(i_d - i))$, and the value $dE_{1/2}/dpH$ are given. Further $E_{1/2}$ values are tabulated for a large number of derivatives. [Ot.So.]

1072 – The polarographic investigation of the transformation of some semi- and thiosemicarbazones in aqueous alcoholic media (in Russian). Yu. P. Kitaev, G. K. Budnikov and A. E. Arbuzov (Chemical Institute, Kazachian Branch of the U.S.S.R. Academy of Sciences, U.S.S.R.). *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk*, (1961) 1222–1227.
The connection between polarographic data and the structure of the substances mentioned has been investigated. Included were derivatives of acetophenone, *p*-chloroacetophenone, *p*-aminoacetophenone and benzophenone. The results show great similarity between the behaviour of semi- and thiosemicarbazones on the Hg drop electrode. $E_{1/2}$ values were determined for these substances under identical conditions of $3 \cdot 10^{-4}$ *M* concentration, pH 5.94, and 3% methanol. The values, as tabulated, lie in the range 1.064 – 1.220. The semicarbazones are reduced at slightly more negative values than the corresponding sulphuric analogues. This is explained by the influence of the electronegative oxygen atom on the electron density of the azomethine group. In slightly alkaline media two waves are observed, corresponding to the existence of two tautomeric forms. [Ot.So.]

1073 – Paper-chromatographic and polarographic determination of vanillin and ethylvanillin in food-stuffs. II (in German). H. Woggon, K. Rauscher and U. Köhler (Institut für Ernährung, Potsdam-Rehbrücke, Berlin, Deutschland). *Nahrung*, 4 (1960) 374–388.
A 5 g sample is extracted with 10 ml of ethanol (abs.) at 45° for 30 min. 0.1 ml of the extract is applied quantitatively to a Whatman 3 MM paper sheet. The chromatogram is developed with *iso*-butanol–conc. NH_3 (5 : 3) for 15 h by the ascending technique. The spots are made visible by u.v. light and eluted with 0.5 *M* semicarbazide HCl in 0.1 *N* HCl. The eluates are polarographed between —0.5 and —1.0 V *vs.* the N.C.E. Vanillin has an R_F 0.33–0.40, and 5–15 μg/ml can be determined with an error of ± 2%. Ethylvanillin has an R_F of 0.51–0.58, and 2–5 μg/ml can be determined with an error of ± 4%. Analyses of various food mixtures are given. [Gio.Ser.]

1074 – Polarographic investigation of quinone-equilibria with interchanged polarisation (in German). E. Bauer and H. Berg (German Academy of Sciences, Berlin, and Institute of Microbiology and Experimental Therapy, Jena, Germany). *Roczniki chem.*, 35 (1961) 329–339.

The electrochemical properties of some substitued 2-N-hydroxyethylbenzoquinones in equilibrium with isomeric ketones, formed during cyclisation are discussed. These compounds were investigated polarographically with interchanged polarisation according to Kalousek and oscillopolarographically by the Heyrovsky method. On polarograms they form two waves, the first one being kinetically limited. From experiments it follows that the first wave corresponds to the reversible reduction of quinone to hydroquinone but contains some contribution from the kinetic current of the ketone. The second wave is the irreversible wave of ketone reduction; the product of this reduction, in contrast to the product of quinone reduction, slowly changes into hydroquinone. [Ad.Hu.]

1075 – Polarographic investigations on the behaviour of *p*-benzoquinone and *p*-benzohydroquinone during the autoxidation of ethyl linolate (in German). K. Täufel, F. Kretzschmann and Cl. Franzke (Institut für Lebensmittelchemie und -technologie der Humboldt-Universität, Berlin, Deutschland). *Mikrochim. Acta*, 2 (1961) 323–331.

Ethyl linolate was exposed to autoxidation in artificial light: (a) in the absence of an inhibitor; and in the presence of: (b) $3.25 \cdot 10^{-3}$ *M* quinone; (c) $1.62 \cdot 10^{-3}$ *M* quinhydrone; (d) $3.25 \cdot 10^{-3}$ *M* hydroquinone. In each case the amount of oxygen consumed (determined by means of a Warburg apparatus) and the concentrations of quinone and hydroquinone (determined by means of a polarograph) were measured as a function of time.

The polarographic wave of the hydroperoxide in the lipid system resulting from the autoxidation does not interfere with the wave of the quinone–hydroquinone system.

In all three cases (b), (c) and (d), after a sufficient time of autoxidation, the inhibitor was transformed completely into quinone. From measurements with the Warburg apparatus it was found, that whereas hydroquinone acts as a true inhibitor, quinone behaves as a "retarder". Quinhydrone can function either as retarder or inhibitor. A more detailed study on the reaction mechanism will appear in *Fette, Seifen, Anstrichmittel*, 62 (1960). [C.I.Moo.]

1076 – Chromatopolarographic investigations. XV. Influence of electrolyte concentration and temperature on the separation of some aliphatic and aromatic nitro compounds on ion exchangers (in Polish). W. Kemula and S. Brzezewski (Department of Inorganic Chemistry, University of Warsaw, Poland). *Roczniki Chem.*, 35 (1961) 711–722.

The influence of electrolyte concentration and temperature on the separation of some aliphatic and aromatic nitro-compounds on ion exchangers was investigated. It was found that the partition coefficient C depends on the molarity M of the salting out solution according to the equation: $\log C = \log C_0 + K_s M$, where K_s represents the salting out coefficient. For ammonium salts, the anion has a pronounced effect on the salting out coefficient — the most positive was found for SO_4^{2-}, the most negative for SCN^-. Elevated temperatures were applied to desorb the compounds strongly retained on the column. It was found that the separation coefficient decreases with the rise of temperature and that its logarithm is a linear function of the temperature. *m*- and *p*-nitrobenzoic acids as well as a mixture of nitroalkanes were separated on the cationite Dowex 50, taking advantage of the desorbing influence of the temperature. The eluate was analysed using the normal chromatopolarographic equipment, at the electric tension—1.0 V *vs.* S.C.E. [Ad.Hu.]

1077 – Polarographic determination of dimethyl and dibutyl phthalates in propellants with use of zinc amalgam to overcome interference from nitroglycerine. J. Townend and E. Macintosh (Naval Ordnance Inspection Laboratory, Caerwent, Chepstow, Monmouthshire, Wales). *Analyst*, 86 (1961) 338–342.

Soxhlet extraction with Et_2O for 7 h separated the phthalate esters and nitroglycerine from the propellant. The Et_2O was evaporated and the residue was dissolved in EtOH and shaken for 1 h with 3% Zn amalgam to reduce nitroglycerine. The mixture was filtered through a No. 4 sintered Buchner funnel. The amalgam was well washed with EtOH. The aliquot of the filtrate and washings was mixed with aqueous tetramethylammonium bromide, titrated with tetramethylammonium hydroxide to the end-point of cresol red and thymol blue, gelatine added and diluted to a fixed volume. After deoxygenation, the polarogram was recorded from —1.4 to —1.8 V against a Hg pool anode. The method was checked by adding known amounts of dimethyl phthalate to synthetic propellants and analyses within 1% of the correct figure were obtained consistently. [P.O.Ka.]

1078 – Polarographic studies of some organo-sulphur compounds. I. A. c. and d.c. polarography of potassium thiobenzoate (in English). K. Okamoto (Research Department, Sankyo Co. Ltd., Shinagawa-Ku, Tokyo, Japan). *Bull. Chem. Soc. Japan*, 34 (1961) 920–924.

Potassium thiobenzoate (PTB) was studied by d.c. and a.c. polarography. Three steps and waves, respectively, were observed; the latter two were due to adsorption processes whilst the most positive process was due to oxidation of PTB to benzoyl disulphide. The redox process was at most slightly reversible, the a.c. wave being quite indistinct. [H.H.Ba.]

1079 – On the use of the chromatopolarographic method for the determination of naphthalene sulphoacids and dinaphthylsulphone (in Russian). A. P. Shestov (Research Institute for Semiproducts and Dyes, U.S.S.R.). *Zhur. Obscheĭ Khim.*, 31 (1961) 1780–1787.
The substances were separated chromatographically on paper, using an eluant mixture of *n*-butyl alcohol–*tert*-butyl alcohol–0.5 *N* HCl (66 : 87.5 : 46.5). Sulpho-acids were eluted by hot water from the chromatogram, cut into strips. The solutions were evaporated, neutralised by *N* $(C_2H_5)_4OH$ and tetraethylammonium-iodide was added as supporting electrolyte to form a 0.05 *M* solution. The solution was made up to 10 ml volume and polarographed. The procedure (including chromatography) involves an error of ± 3%. [Ot.So.]

1080 – A polarographic investigation of perinaphthenone. The late P. Beckmann (c/o B. Breyer, Faculty of Agriculture, The University of Sydney, Australia). *Australian J. Chem.*, 14 (1961) 229–236.
Perinaphthenone gives two one-electron polarographic steps, the first reversible and the second irreversible. Adsorption steps are produced between these two steps and, in alkaline solutions, after the second main reduction step. The rate of decomposition of the free radical produced in the first stage of reduction was measured by electrolysis to produce the radical and potentiometric measurement of its rate of disappearance.
Preliminary results with 6-hydroxy- and with 9-carboxyperinaphthenone-7 are also reported. [H.H.Ba.]

1081 – Polarographic determination of anthracene, phenanthrene and carbazole in products of the coal industry (in Russian). A. G. Pozdeeva (Research Institute of the Coal Industry, Sverdlovsk, U.S.S.R.). *Zhur. Priklad. Khim.*, 34 (1961) 1842–1849.
The method of derivative polarography was employed, measurements being carried out on an electronic polarograph. The supporting electrolyte was a 0.1 *M* solution of tetrabutylammonium iodide in 75% dioxane. An electrolytic vessel with an inner anode was used. The electric tension of the anode in the above named electrolyte was 0.41 V *vs.* S.C.E. $E_{1/2}$ values were: anthracene; —2.17 for the first, and —2.45 for the second peak; phenanthrene; — 2.65 for the first, and —2.86 for the second peak; carbazole; —2.89. (All values in volts, S.C.E.) Up to 0.6 mg/ml concentration, peak heights are proportional to concentration. Details of the possibility of determining various products are given. Precision is 1.0–5.0%, rel. [Ot.So.]

1082 – Polarographic determination of frangula emodin in cholagole (in Czech). J. Frgala (Galena Works, Komárov, Czechoslovakia). *Českoslov. farm.*, 10 (1961) 344–346.
2 ml of the pharmaceutical are mixed in a 100 ml beaker with 25 ml of a fresh 4 *M* ethanolic KOH solution and boiled 30 min under reflux. After cooling, the mixture is diluted with water to volume in a 50 ml volumetric vessel. 25 ml of this solution are transferred into a Kalousek-type polarographic vessel and bubbled 6 min with nitrogen. A polarogram is then registered from —0.6 V. Then 1 ml of the standard solution is added and after repeated bubbling a second polarogram is registered. Errors are ± 2%. [Ot.So.]

1083 – On the electrochemical behaviour of pyridine (in Russian). G. A. Tedoradse and S. G. Mayranovskii (Institute of Electrochemistry, Academy of Sciences, U.S.S.R.). *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk*, (1961) 1352–1354.
In the reduction of pyridine on the mercury drop electrode, pyridine is reduced to a surface-active polymeric product simultaneously with the evolution of hydrogen. The enhancement of the catalytic wave in pyridine solutions with time is caused by the catalytic action of the product being adsorbed on the drop surface. [Ot.So.]

1084 – A.c. polarography of thiamine hydrochloride in weakly acidic buffer solutions (in English). K. Okamoto (Research Department, Sankyo Co. Ltd., Shinagawa-Ku, Tokyo, Japan). *Bull. Chem. Soc. Japan*, 34 (1961) 1063–1067.
No well-defined d.c. steps of thiamine were obtained in neutral or weakly acid buffer solutions, but clearer a.c. waves were observed–one wave at — 1.27 to —1.32 V *vs.* S.C.E. at pH 3–5, two waves at —1.27 to —1.32 and —1.33 to —1.46 V *vs.* S.C.E. respectively at pH 5–9, and no waves in more alkaline solutions. Variation of wave-height with temperature, mercury-reservoir height and concentration indicated diffusion-controlled processes. [H.H.Ba.]

1085 – Investigation of some factors affecting polarographic catalytic waves (in German). E. Pungor and Gy. Farsang (Institute of Inorganic and Analytical Chemistry, Eötvös University, Budapest, Hungary). *Ann. Univ. Sci. Budapest. Rolando Eötvös nominatae, Sect. Chim.*, 2 (1960) 293–298.

For the case of quinine and vitamin B_1, the effect of buffer concentration, catalyst concentration and pH value on the catalytic hydrogen wave was investigated. The maximum current value was achieved in various buffer dilutions at quite different pH values. Similarly, it was found in the case of vitamin B_1, that the wave height of catalyst concentration varies according to a curve of maximum type. The presence of alien electrolytes leads to a decrease in the catalytic wave. From these observations, the authors concluded that adsorption on the electrode plays a marked role in the formation of the catalytic wave. [E.Pun.]

1086 – Estimation of riboflavin by a.c. polarography. B. Breyer and T. Biegler (Section of Agricultural Chemistry, Department of Agriculture, University of Sydney, Australia). *J. Electroanal. Chem.*, 1 (1959/1960) 453–457.

A.c. polarography can be successfully used to determine riboflavin, in concentrations as low as $2 \cdot 10^{-7}$ *M*, in pharmaceutical preparations and biological materials, including milk. An acetate buffer of pH 4.7 is recommended as the supporting electrolyte when the riboflavin concentration lies between 10^{-6} *M* and 10^{-5} *M*. For smaller concentrations, a borate buffer, pH 9.5, is preferable. The accuracy of the method is about $\pm$ 10% in the concentration range below 10^{-6} *M* and about $\pm$ 2% in the higher concentration range. Since the estimation can be carried out in air, the method is particularly speedy. [Authors]

1087 – Polarographic study of the nonenzymatic hydrolysis of pyridoxal-5-phosphate (in English). P. Zuman and O. Manoušek (Polarographic Institute, Czechoslovak Academy of Sciences and Central Food Research Institute, Prague, Czechoslovakia). *Collection Czechoslov. Chem. Communs.*, 26 (1961) 2134–2144.

The rate constant of the hydrolysis of pyridoxal-5-phosphate has been followed in aqueous solutions at pH 1–4, $\mu = 1.0$ at 60°–90°. Polarographic measurement of the rate of hydrolysis was based on the difference in behaviour of pyridoxal-5-phosphate and of pyridoxal in acid medium. The half-wave electric tensions of the two substances mentioned do not differ sufficiently to make a separation of the two waves possible. In a mixture only one wave is observed. The limiting current of pyridoxal-5-phosphate is diffusion controlled and pH-independent, whereas pyridoxal shows, in the pH region 1–4, only a small limiting current (10–30% of the theoretical diffusion current). This current is kinetic. Procedure: 9.75 ml of the medium–buffer or perchloric acid plus sodium perchlorate were deaerated, 0.25 ml of a 0.02 *M* stock solution of pyridoxal-5-phosphate was added, and after deaeration, curves were recorded in intervals of 10–30 min. After each run curves for pyridoxal were recorded under identical conditions. [Ot.So.]

1088 – Polarographic determination of pyridoxal and pyridoxal-5-phosphate (in German). O. Manousek and Peter Zuman (Polarographic Institute, Czechoslovak Academy of Sciences and Central Food Research Institute, Prague, Czechoslovakia). *J. Electroanal. Chem.*, 1 (1959/1960) 324–330.

The estimation of pyridoxal together with pyridoxal-5-phosphate has been carried out by two polarographic methods. The first method is based on the varying heights of the pyridoxal waves between pH 2 and 9. Since the height of the wave of the pyridoxal-5-phosphate practically does not alter with pH, the decrease in the wave height of a mixture of the two compounds at pH 2 is proportional to the pyridoxal concentration. The concentration of both components can be evaluated from i_1 (at pH 2) and i_2 (at pH 9) with the aid of given equations.

The second method is based on the conversion of both components into the pyridoxaloxime and the pyridoxaloxime-5-phosphate. The half-wave values of the oxime waves differ in Veronal buffer at pH 9 by 80 mV, which is a sufficient difference to enable the separate waves to be measured by means of the outgoing current. With this method a $3 \cdot 10^{-5}$ *M* solution of pyridoxal in a 50-fold excess of pyridoxal-5-phosphate can be estimated. The presence of additional substances such as pyridoximes, pyridoxamines, etc. does not interfere. [Authors]

1089 – Polarographic investigations of vitamin C. III. Reduction waves of condensation products of dehydro-L-ascorbic acid and its derivatives with *o*-phenylenediamine. Application to simultaneous determination of L-ascorbic acid, dehydro-L-ascorbic acid and related compounds (in English). T. Wasa, M. Takagi and S. Ono (College of Agriculture, University of Osaka Prefecture, Sakai, Osaka, Japan). *Bull. Chem. Soc. Japan*, 34 (1961) 518–528.

Dehydro-L-ascorbic acid (DAA) showed three diffusion-controlled polarographic steps whose height depended on pH, temperature, concentration of added *o*-phenylenediamine (OPD) and time after the addition of OPD. In solutions containing DAA and L-ascorbic acid (AA), the oxidation wave of AA could be measured without interference by the three steps of DAA.

2,3-diketogulonic acid (DGA) showed two steps, the first being close to the first step of DAA and the second apparently identical with the second step of DAA; the rate of condensation of DGA with OPD was much less than that of DAA and OPD.
Alloxan and dehydroreductic acid (DRA) gave single well-defined reduction steps; reductic acid (RA) showed an oxidation step which could be measured in the presence of DRA; the oxidation wave of dialuric acid decreased rapidly on addition of alloxan and OPD in air-free solution. Mesoxalaldehyde (MOA) gave smaller and ill-defined steps in acid solution. Simultaneous estimation was possible of AA and DAA; of RA and DRA; of AA and RA; and alloxan could be determined also. MOA and DGA could not be determined by this method, but their presence did not interfere with estimation of DAA or AA. [H.H.Ba.]

1090 – Polarographic determination of 1-(2'-hydroxyethyl)-2-methyl-5-nitroimidazole (in Polish). A. Danek (Department of Inorganic and Analytical Chemistry, Academy of Medicine, Kraków, Poland). *Dissertationes Pharm.*, 13 (1961) 107–110.
It was found that the polarographic reduction of the nitrogroup of 1-(2'-hydroxyethyl)-2-methyl-5-nitroimidazole can be used for the determination of this compound. Of the two polarographic reduction waves the first one is well developed in acetate media and its height in the range 0.02–0.1 mg/ml is proportional to the concentration. $E_{1/2}$ = —0.24 V *vs.* S.C.E. As a supporting electrolyte 1 *N* KCl was used containing 0.02% gelatine. The standard deviation of the method was 0.0113 mg. This method can be used for the analysis of both the pure substance and tablets. [Ad.Hu.]

1091 – Polarographic determination of phenolphthalein and santonine when present together in santonine-chocolate (in Czech). M. Traiter (Slovakofarma Works, Hlohovec, Czechoslovakia). *Českoslov. farm.*, 10 (1961) 352–353.
One portion of the sample is extracted in a 100 ml volumetric flask by 96% ethyl alcohol, while heating gently. The mixture is then left to stand for 4–5 hours. After making up to volume with alcohol and filtering, 25 ml of the extract is transferred into another 100 ml volumetric flask and made up to volume with 4 *N* HCl. In this operation the mixture becomes turbid and must be filtered again. An aliquot of this solution is bubbled with hydrogen and a polarogram is registered from —0.2 V *vs.* S.C.E. Results are calculated by comparison with a standard. [Ot.So.]

1092 – Polarographic behaviour of methylene blue, with particular respect to its catalytic wave (in German). E. Pungor and Gy. Farsang (Institute of Inorganic and Analytical Chemistry, Eötvös University, Budapest, Hungary). *Ann. Univ. Sci. Budapest. Rolando Eötvös nominatae, Sect. Chim.*, 2 (1960) 299–304.
The catalytic wave of methylene blue depends to a great extent on the degree of buffer dilution. Depending on the concentration of methylene blue, the curve of buffer dilution may be a monotonous or a maximum shape. Foreign salts, *e.g.* potassium bromide, decrease the catalytic wave to a great extent. However, it was found that the maximum values of the buffer dilution curve plotted at an identical pH value, and in an identical concentration of methylene blue, in the presence and absence, respectively, of a foreign salt, appeared in the same region of buffer dilution. Thus, the absorption of catalyst and of buffer components is affected by foreign salts in an approximately identical way. [E.Pun.]

1093 – Chemical changes occurring at the adsorption of metanil yellow and methylene blue (in German). E. Pungor and E. Hollós-Rokosinyi (Institute of Inorganic and Analytical Chemistry, Eötvös University, Budapest, Hungary). *Ann. Univ. Sci. Budapest. Rolando Eötvös nominatae, Sect. Chim.*, 2 (1960) 17–21.
Starting from the theory of adsorption indicators, the ability of metanil yellow to be adsorbed on silver halides was studied by the authors. Further, the behaviour of methylene blue on the surface of the dropping mercury electrode was investigated. These investigations were carried out according to Knobloch. It was found that differences are perceptible in the dissociation constant of methylene blue measured by polarography in various electrolytes. From these, conclusions were drawn with respect to the adsorption characteristics of methylene blue adsorbed by the electrode. The proton binding ability of the dye proved to decrease, due to the content of positive ions in the surface layer, which is determined by the period of life of the active form. [E.Pun.]

1094 – The application of alternating-current polarography in the determination of phenobarbitone in dosage forms. N. G. Lordi, E. M. Cohen and B. L. Taylor (College of Pharmacy, Rutgers State University, Newark, N. J., U.S.A.). *J. Am. Pharm. Assoc., Sci. Ed.*, 49 (1960) 371–375.
Phenobarbitone (0.2–0.4 mg) is dissolved in 25 ml of borate buffer of pH 7.9 containing 1*M* KNO_3. The solution is polarographed at a scanning rate of 0.00062 V/sec, applying an alternating current

of 0.03 V rev/msec. The concentration is calculated by measuring the peak current and comparing it with a standard curve. ± 2% accuracy can be obtained. Caffeine, diphenylhydantoin, aminophylline, theobromine sodium salicylate, thiamine, polyoxyethylene glycol 400 and halides interfere with the determination. [Gio.Ser.]

1095 – Investigation of the polarographic and adsorptive properties of benzoyl derivatives of some barbiturates (in Russian). K. R. Voronova and A. G. Stromberg (Polytechnic Institute, Tomsk, U.S.S.R.). *Zhur. Obscheĭ Khim.*, 31 (1961) 2786–2792.
10 derivatives of barbituric acid, used as pharmaceuticals, were investigated. It is shown that the first polarographic wave in six of the substances is of an adsorptive character. On investigating their electrocapillary curves, it was found that six of the derivatives, which give polarographic waves, decrease surface tension. Benzoyl derivatives decrease the surface tension of mercury more effectively, and in a broader range of potentials. It is shown that in the concentration range 10^{-6}–10^{-3} M, the dependence of the relative decrease of the oxygen maximum on the logarithm of concentration has the form of straight lines, intersecting at one point. [Ot.So.]

1096 – Notes on the polarographic determination of morphine present in the initial substances and concentrates of morphine manufacture (in German). E. Schulek and K. Burger (Institute of Inorganic and Analytical Chemistry, Eötvös University, Budapest, Hungary). *Ann. Univ. Sci. Budapest. Rolando Eötvös nominatae, Sect. Chim.*, 2 (1960) 531–536.
On applying the polarographic method suggested by Rasmusen, the authors investigated the suitability of a hydrochloric acid solution of *n*-propanol as a solvent. The results obtained were controlled by comparing them with those yielded by the Schulek method of morphine determination. [E.Pun.]

1097 – Polarography of narcotine-N-oxide (in English). Y. Asahi (Research Laboratory, Takeda Pharmaceutical Industries Ltd., Osaka, Japan). *Bull. Chem. Soc. Japan*, 34 (1961) 1185–1188.
Narcotine-N-oxide was studied by d.c. and a.c. polarography. A catalytic hydrogen step, with corresponding a.c. wave, was observed; there was no a.c. wave corresponding to the 2-electron reduction of the oxide to narcotine. It is concluded that the first step involves adsorption of the reductant and that adsorbed films hinder further reduction, leading to anomalous "minimum waves" at high depolarizer concentrations. The second step at pH 1–5 corresponds to the proton adduct of the N-oxide with lactone, and the 3rd step at pH 5–10 to the base of the N-oxide. [H.H.Ba.]

1098 – Polarography in pharmaceutical analysis. IV. Determination of hormones (in Polish). R. Stareścik (Department of Inorganic Chemistry, Academy of Medicine, Wroclaw, Poland). *Farm. Polska*, 16 (1961) 28.
A review with 44 references. [Ad.Hu.]

1099 – Polarographic behaviour of mesobilirubin (in German). B. Tvaroha (Medical Clinic, Charles University, Prague, Czechoslovakia). *Collection Czechoslov. Chem. Communs.*, 26 (1961) 2271–2278.
Mesobilirubin is soluble in aqueous alkaline buffers forming three polarographic waves, one anodic and two cathodic. The first cathodic wave is capacity controlled, being rather a prewave caused by capacity changes of the electric double layer of the drop electrode conditioned by the electric tension. The second diffusion-controlled wave corresponds to a four-electron reduction of mesobilirubin to mesobilirubinogen: its height and half-wave tension are pH-independent at pH values above 9.0; $E_{1/2}$ is —1.62 V *vs.* S.C.E. The anodic wave corresponds to a reaction of mesobilirubinogen with electrode mercury which is also a four-electron process. [Ot.So.]

See also abstracts nos. 957, 958, 959, 972, 973, 974, 980, 982, 987, 993, 1117, 1134, 1150, 1223, 1260.

4. Potentiometry

1100 – Stability of metal-ion complexes in solution. I. Potentiometric methods for computing successive stability constants of mononuclear complexes (in Polish). L. Pajdowski

(Department of Inorganic Chemistry, The University, Wroclaw, Poland). *Wiadomości chem.*, 15 (1961) 369–402.
A review article, which contains a description and discussion of methods of stability determination of complexes in solution. 43 references. [Ad.Hu.]

1101 – Stability of metal-ion complexes in solution. II. Potentiometric methods for computing stability constants of polynuclear two-component complexes ($A_p B_q$) (in Polish). L. Pajdowski (Department of Inorganic Chemistry, The University, Wroklaw, Poland). *Wiadomości chem.*, 15 (1961) 463–481.
A review, concerning problems related to formation and stability of polynuclear complexes. 31 references. [Ad.Hu.]

1102 – Potentiometric determination of metallic oxides: solubilities in fused sodium metaphosphate (in Russian). Yu. K. Delimarski and V. N. Andreeva (Institute of General and Inorganic Chemistry, Academy of Sciences, Ukraine, S.S.R.). *Dopovidi Akad. Nauk Ukr. R.S.R.*, 5 (1959) 633.
By means of a porcelain triangle, a porous porcelain crucible containing a $PbO-NaPO_3$ mixture is held concentrically in a second, larger, $NaPO_3$-containing crucible; Pt electrodes are introduced through porcelain tubes into the crucibles. The whole system is held at a constant temperature of 720°, and the electric tensions are read against a $Pt-O_2$ electrode. By plotting the tension against the log of the molar ratio of the solute, a value of 31.6 mol % is obtained in agreement with the value obtained from the isothermal saturation method (31.0%); the procedure, which gives constant and reproducible results, can be applied to other oxides. [Ca.Cas.]

1103 – Thermodynamic properties of some metal oxides dissolved in molten sodium metaphosphate (in Russian). V. N. Andreeva and Yu. K. Delimarski. *Zhur. Neorg. Khim.*, 5 (1960) 2076–2083.
The thermodynamic properties of solutions of Bi, Ni, Mo and Sb oxides in melted $NaPO_3$ have been derived from determinations of the electric tension of the following cells:
(1) $Bi/NaPO_3 \cdot Bi_2O_3(N)/O_2(Pt)$; mol. fraction N from 0.01 to 1.00, and temperature range 720°–960°;
(2) $Ni/NaPO_3-NiO(N)/O_2(Pt)$; mol. fraction N from 0.005 to 1.00, and temperature range 720°–900°;
(3) $Mo/NaPO_3-MoO_3(N)(O_2(Pt)$; mol. fraction N from 0.01 to 1.00, and temperature range 720° 900°;
(4) $Sb/NaPO_3-Sb_2O_3(N)/O_2(Pt)$; mol. fraction N from 0.01 to 0.40, and temperature range 720°–860°. [Li.Ne.Ro.]

1104 – Method for the determination of the equivalence point in potentiometric titrations (in English). J. M. H. Fortuin (Central Laboratory, Staatsmijnen in Limburg, Geleen, The Netherlands). *Anal. Chim. Acta.*, 24 (1961) 175–191.
The author has developed an accurate method which can be applied to symmetrical potentiometric titrations. The method is simple, requires no graphical representations of the experimental results and possesses a theoretical basis. In addition, it gives approximate values for the ionization constant of the slightly dissociated substances formed during the titration. The influence of dilution is also studied. The method is compared with the procedure of Kolthoff and that of Hahn. [P.Me.]

1105 – The use of the dynamic condenser method for measurement of electric tensions on solid insulator–water solution interfaces (in English). A. Waksmundzki and Z. Ratajewicz (Department of Physical Chemistry of Surface Phenomena, Institute of Physical Chemistry, Polish Academy of Sciences, Lublin, Poland). *Bull. acad. polon. sci., sér. sci. chim.*, 9 (1961) 451–453.
The dynamic condenser method can be used for measurements of electric tension on the solid insulator–solution interface. The accuracy of tension measurement is better than 15 mV. The presence of electrolytes in the aqueous solution shifts the tension towards more positive values, and of nonelectrolytes, towards negative values. Particularly great tension changes were observed in the case of 0.01 M laurylamine hydrochloride. [Ad.Hu.]

1106 – Measurement of activity coefficients and transference numbers in aqueous NaCl solutions (in Italian). R. Caramazza (Institute of General Chemistry, University of Naples, Italy). *Gazz. chim. ital.* 90 (1960) 1839–1846.
By using the same apparatus and methods as in previous works on KCl (*Gazz. chim. ital.*, 90 (1960) 1721, 1730), activity coefficients and transfer numbers were determined in 0.001–5 M NaCl at 0°, 18°, 25°, 35° and 50°. See also Abstract Nos. 1107 and 1108. [Fr.Pan.]

1107 – Measurement of activity coefficients of KCl in aqueous solutions (in Italian). R. Caramazza (Institute of General Chemistry, University of Naples, Italy). *Gazz. chim. ital.*, 90 (1960) 1721–1729.
Electric tension measurements were performed using the cell:

$$Ag \mid AgCl \mid KCl_{(x)} \mid K(Hg) \mid KCl(0.1\ N) \mid AgCl \mid Ag$$

without liquid junction, at 18° and 50°, in the range 0.05–4 *M* KCl. The activity coefficients were derived by the Hückel equation. [Fr.Pan.]

1108 – Determination of thermodynamic friction coefficients of KCl in aqueous solutions at several temperatures (in Italian). V. Vitagliano and R. Caramazza (Institute of Physical Chemistry, University of Naples, Italy). *Gazz. chim. ital.*, 90 (1960) 1730–1745.
The transference numbers were determined potentiometrically in 0.01–4 *M* KCl at 0°, 18°, 25°, 35° and 50°. The diffusion coefficients in the same solutions were determined interferometrically. The thermodynamic friction coefficients were also derived. [Fr.Pan.]

1109 – Noble metal/cyanhydric acid electrodes (in Italian). E. Paglia Dubini and E. Padula (Centro di Chimica Metallurgica del C.N.R., Università di Milano, Italy). *Atti accad. naz. Lincei.*, 28 (1960) 63–68.
Experimental values of electrode electric tensions (E.T.) for electrodes obtained with Au, Ag, Hg, Pd or Pt dipped in buffer solutions saturated with HCN are given. Values are measured in an atmosphere of argon against a quinhydrone electrode. The electric tensions are proportional to the pH of the solution, the slope of the curves being different for each metal. For Hg and Au the relationship between E.T. and HCN concentration is studied; the effect of $Hg(CN)_2$ concentration on the E.T. is investigated in the particular case of the Hg electrode, keeping both pH and HCN concentration constant. It seems that traces of O_2 in the buffer solution speed up the establishment of the electric tensions. [Su.Mo.Ce.]

1110 – The assay of sodium citrate and sodium potassium tartrate by cation exchange and non-aqueous titrimetry. M. L. Richardson (John E. E. Sturge Limited, Lifford Chemical Works, Kings Norton, Birmingham, Great Britain). *Anal. Chim. Acta*, 24 (1961) 46–54.
A direct measure of the anion content of sodium citrate and sodium potassium tartrate is obtained by passing aqueous solutions of the salts through cation exchange resin columns, concentrating the effluents from the columns, and then titrating the effluents with standard sodium hydroxide solution. The direct measure of the cation content of sodium citrate is obtained by titrating a solution of the salt in glacial acetic acid with standard acetous perchloric acid, the end-point being detected potentiometrically. A modification of this method is used for sodium potassium tartrate: the salt is stirred in excess acetous-perchloric acid, the excess of which is back titrated with standard acetous-potassium acetate. The maximum error for this methods is of the order of 0.2%. [P.Me.]

1111 – Studies on the behaviour of uni-bivalent salts in aqueous solution. I. K, NH_4, Na, and Li sulphates and determination of standard electrode potential of $Hg/Hg_2SO_4,SO_4^{2-}$ (in English). S. C. Sircar, P. K. Jena and B. Prasad (Ravenshaw College, Cuttack, India). *J. Indian Chem. Soc.*, 38 (1961) 101.
The electric tension of the cells of types a, b, c, and d have been calculated. In these cells "M" stands for K, NH_4, Na and Li and "C" for concentration in g moles/l. A study of the cells a and b shows that sulphates of potassium, ammonium, sodium and lithium are completely dissociated in aqueous solution up to 0.1 *M*. The standard electrode tension of the half cell, $Hg/Hg_2SO_4,SO_4^{2-}$ has been found to be —0.6025 V at 35°.

$$\text{(a)}\quad \underset{(C_2)}{Hg/M_2SO_4,Hg_2SO_4}//\text{salt bridge}//\underset{(C_1)}{Hg_2SO_4,M_2SO_4/Hg}$$

$$\text{(b)}\quad \underset{(C_2)}{Hg/M_2SO_4,Hg_2SO_4}//\underset{(C_1)}{Hg_2SO_4,M_2SO_4/Hg}$$

$$\text{(c)}\quad \underset{(C)}{Hg/M_2SO_4,Hg_2SO_4}//\text{saturated KCl bridge}//\underset{(2C)}{Hg_2Cl_2,MCl/Hg}$$

$$\text{(d)}\quad \underset{(C)}{Hg/M_2SO_4,Hg_2SO_4}/\underset{(2C)}{Hg_2Cl_2,MCl/Hg}.$$

[R.S.Sa.]

1112 – The oxidation–reduction potentials of some copper complexes. B. R. James and R. J. P. Williams (The Inorganic Chemistry Laboratory, Oxford, Great Britain). *J. Chem. Soc.*, (1961) 2007–2019.

The method used is based on the construction of diagrams in which the electric tensions measured are plotted against the pH meter readings for solutions equimolar in Cu(I) and Cu(II) in the presence of excess of various complexing agents (mostly substituted 1,10-phenanthrolines, bipyridyls and other nitrogen donors). The fact that there is no simple relation between the redox tensions of the complexes and the acid dissociation constant of the complexant is interpreted in terms of change in co-ordination number, relative to the nature of the ligand; the factors determining the value of this number are considered and discussed, and the behaviour of Cu(II) is compared with that of cations (Ca^{2+}, Ni^{2+}) of different polarising power. [L.Gi.]

1113 – The complex formation between copper(II) ion and methoxyacetate, ethoxyacetate, (ethylthio)acetate, and thiodiacetate ions (in English). Arvid Sandell (Department of Inorganic and Physical Chemistry, Chemical Institute, University of Lund, Sweden). *Acta Chem. Scand.*, 15 (1961) 190–210.

The complexing constants of the mononuclear complexes formed by copper(II) ion in water solution with methoxyacetate, ethoxyacetate, (ethylthio)acetate, and thiodiacetate ions have been determined by potentiometric methods at 20.0°. The investigations have been carried out in a perchlorate medium at ionic strength $I = 1.0\ M$. The relevant numerical data are collected in Tables A and B.

TABLE A

The logarithms of the complexing constants determined at 20.0° and ionic strength 1.00 *M*

System	$\log \beta_1$	$\log \beta_2$	$\log \beta_3$	$\log \beta_4$
Cu^{2+}–$Me{\cdot}O{\cdot}CH_2{\cdot}COO^-$	1.82	2.81	3.11	2.8
Cu^{2+}–$Et{\cdot}O{\cdot}CH_2{\cdot}COO^-$	1.79	2.87	3.20	2.8
Cu^{2+}–$Et{\cdot}S{\cdot}CH_2{\cdot}COO^-$	2.56	4.76	4.85	—
Cu^{2+}–$S(CH_2{\cdot}COO^-)_2$	4.18	7.08	8.6	11.9

TABLE B

The stability constants calculated from the determined complexing constants

System	b_1 (M^{-1})	b_2 (M^{-1})	b_3 (M^{-1})	b_4 (M^{-1})	$\frac{b_1}{b_2}$	$\frac{b_2}{b_3}$	$\frac{b_3}{b_4}$
Cu^{2+}–$Me{\cdot}O{\cdot}CH_2{\cdot}COO^-$	66	9.7	2.0	0.46	6.8	4.9	4.3
Cu^{2+}–$Et{\cdot}O{\cdot}CH_2{\cdot}COO^-$	62	11.9	2.2	0.38	5.2	5.4	5.8
Cu^{2+}–$Et{\cdot}S{\cdot}CH_2{\cdot}COO^-$	365	160	1.2	—	2.3	130	—
Cu^{2+}–$S(CH_2{\cdot}COO^-)_2$	15,000	800	33	2000	19	2.4	0.02
Cu^{2+}–$CH_3{\cdot}COO^-$ (according to Fronaeus)	47	9.6	2.6	0.65	4.9	3.7	4.0

β_n is the complexing constant and the index n is the value of the ligand number;
b_n is the stability constant and the index n is the value of the ligand number. [Sv.Li.]

1114 – Formation of copper complexes of 1,2-diaminopropane in aqueous solutions (in English). Reino Näsänen and Paavo Meriläinen (Department of Chemistry, University of Helsinki, Finland). *Suomen Kemistilehti*, 34 B (1961) 47–49.

The formation of a complex between copper ion and 1,2-diaminopropane in aqueous sodium perchlorate solution has been studied potentiometrically. The values 10.54, 10.65, 10.85, 11.05 and 11.37 were obtained for the logarithm of the first stability constant at 25° at ionic strengths 0, 0.1, 0.5, 1 and 2. The corresponding values for the logarithm of the second stability constant are 19.60, 19.84, 20.32, 20.78 and 21.45. The acid dissociation constants of diprotonated 1,2-diaminopropane in sodium perchlorate solutions were determined. The relevant data are summarized in the following table.

Equilibrium constants K_I and K_{II} for copper complexes of 1,2-diaminopropane in sodium perchlorate solutions at 25°.

I	pK_I	pK_{II}
0.0252	6.009	7.480
0.0388	6.019	7.495
0.500	6.194	7.561
1.00	6.298	7.624
2.02	6.452	7.745

[Sv.Li.]

1115 – Complexes of Cu^{2+} with the acids $S[(CH_2)_nCOOH]_2$ (in Italian). E. Campi, G. Ostacoli, N. Cibrario and G. Saini (Institute of Analytical Chemistry, University of Turin, Italy). *Gazz. chim. ital.*, 91 (1961) 361–367.
Following previous works on the same subject, the authors determined potentiometrically the stability constants (at 20° and ionic strength 0.1) of the 1 : 1 complexes between Cu^{2+} and $S[(CH_2)_n COOH]_2$ (n = 1,2). A general discussion is included on the stability of similar complexes. [Fr.Pan.]

1116 – Complexes of Cu^{2+} with dicarboxylic acids: $(CH_2)_n[S(CH_2)_mCOOH]_2$ (in Italian). G. Ostacoli, E. Campi, N. Cibrario and G. Saini (Institute of Analytical Chemistry, University of Turin, Italy). *Gazz. chim. ital.*, 91 (1961) 349–360.
A potentiometric determination has been carried out of the stability constants of the complexes formed betweed Cu^{2+} and $(CH_2)_n[S(CH_2)_mCOOH]_2$, ($n$ = 0.1,2,3; m = 1,2) at 20° and ionic strength 0.1. Complexes with a molar ratio 1 : 1, such as CuA and CuA^+(H_2A being the acid) are evident in each case, with the largest stability constants when penta-atomic rings are formed. [Fr.Pan.]

1117 – Potentiometric and amperometric titration with EDTA: Hg and Cu electrodes (in French). Georgette Guérin, Jean Desbarres et Bernard Tremillon (Laboratoire de Chimie Analytique, Ecole de Physique et de Chimie, Paris, France). *J. Electroanal. Chem.*, 1 (1959/1960) 226–240.
Electrochemical phenomena at mercury and copper electrodes in various media and in the presence of ethylenediaminetetraacetic acid or its complexes with metallic cations, were studied by plotting the current–electric-tension curves. The corresponding electrochemical reactions were found to be fairly rapid in acid medium, but slow in ammoniacal media.
The various possibilities of titrating mercuric ions with mercury electrodes, and cupric ions with copper electrodes, were investigated. The titration curves were interpreted on the basis of current–electric tension curves. The possibility of titrating cations that are not electroactive or those that are difficult to reduce — such as ions — was also examined by means of current–electric tension curves. [Authors]

1118 – Potentiometric study of reactions of cuprous salts with some oxidizing agents (in English). Ludmilla Suchomelová, Jan Doležal and Jaroaslav Zýka (Department of Analytical Chemistry, Charles University, Prague, Czechoslovakia). *J. Electroanal. Chem.*, 1 (1959/1960) 403–407.
A burette connected to a silver reductor has been suggested for use with a solution of cuprous salt as a reductometric reagent without the use of an inert atmosphere. The reactivity of the cuprous salt with various oxidizing agents was studied and conditions were found for the quantitative reduction and potentiometric titration of Fe^{3+}, Ce^{4+}, VO_3^-, $Cr_2O_7^{2-}$, $Fe(CN)_6^{2-}$ and IO_3^-. [Authors]

1119 – Titration of weak acids using an aluminium electrode (in English). Elio Scarano and Sandro Signoretti (Institute of Analytical Chemistry, University of Rome, Italy). *J. Electroanal. Chem.*, 1 (1959/1960) 218–225.
The possibility of using an aluminium electrode as an indicator electrode in strongly alkaline media (beyond pH 9) for potentiometric titrations of weak acids, has been investigated.
Rapid titrations of NaOH in mixtures of NaOH and Na_2CO_3, with HCl, and of $NaHCO_3$ in mixtures of $NaHCO_3$ and Na_2CO_3, with NaOH, in partially deoxygenated media have been performed. [Authors]

1120 – Determination of standard electrode potential of $Ag/Ag_2CrO_4,CrO_4^{2-}$ electrode (in English). P. K. Jena and B. Presad (Ravenshaw College, Cuttack, India). *J. Indian Chem. Soc.*, 37 (1960) 634.

The standard electrode tension of the Ag/Ag_2CrO_4, CrO_4^{2-} electrode has been determined from the e.m.f. values of the following types of cells:

$$\text{(a)}\quad Ag \mid \underset{(C)}{Ag_2CrO_4, K_2CrO_4} \parallel \text{salt bridge} \parallel \underset{(C)}{K_2SO_4, Hg_2SO_4} \mid Hg;$$

$$\text{(b)}\quad Ag \mid \underset{(C)}{Ag_2CrO_4, K_2CrO_4} \mid \underset{(C)}{K_2SO_4, Hg_2SO_4} \mid Hg.$$

The most probable value of the electrode tension obtained is —0.4468 V at 35°. [R.S.Sa.]

1121 – Studies on the citrate complex of beryllium (in English). R. K. Patnaik and S. Pani (College of Engineering, Sambalpur, Orissa, India). *J. Indian Chem. Soc.*, 38 (1961) 233.
The citrate complex of beryllium has been studied in the pH range of 2.6–6.0. Beryllium ion reacts with citric acid and forms in the lower pH region a neutral complex (C) liberating two protons according to the reaction:

$$Be^{2+} + H_3Cit \rightarrow C + 2\,H^+ \qquad (1)$$

In the higher pH range this neutral complex dissociates like a dibasic acid to give the complexes C_1^- and C_2^{2-} according to the following reactions

$$C \rightleftharpoons C_1^- + H^+ \qquad (2)$$

$$C_1^- \rightleftharpoons C_2^{2-} + H^+ \qquad (3)$$

The equilibrium constants of reactions 1,2 and 3 are found to be $4.52 \cdot 10^{-4}$, $2.41 \cdot 10^{-4}$, and $4.95 \cdot 10^{-6}$ respectively. [R.S.Sa.]

1122 – Complex compounds of beryllium with 5-nitrosalicylic acid (in English). Mary Abraham and S. N. Srivastav (University College of Science, Calcutta, India). *J. Indian Chem. Soc.*, 37 (1961) 477.
The complex formation between nitrosalicylic acid and beryllium nitrate has been studied by pH and conductance measurements and the effect of the nitro group on the chelation of ions has been investigated. pH and conductance graphs were plotted showing the effect of dropwise addition of $M/2$ KOH on mixtures of beryllium nitrate containing 0,1,2 and 3 moles respectively of the potassium salt of 5-nitrosalicylic acid. The results show the formation of only one complex (1 : 1) at pH 4. The absence of a higher complex obtained in the case of salicylic acid indicates that the nitro group hinders chelation. [R.S.Sa.]

1123 – Metal complexes of bis-[3-di(carboxymethyl)aminopropyl]ether. The calculation of stability constants with the aid of a high-speed digital computer. H. Irving and M. H. Stacey (Inorganic Chemistry Laboratory, The University, Oxford, Great Britain). *J. Chem. Soc.*, (1961) 2019–2027
Stability constants for Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Zn^{2+}, Cd^{2+} and Hg^{2+} have been determined at 20° and $\mu = 0.1$ KCl, from pH metric curves. The calculation of the results has been performed by the method of successive approximation, using a high-speed digital computer. The sequence found for the various constants is compared with that found with homologous complexones, and some anomalies are discussed in terms of structure. [L.Gi.]

1124 – Studies on the citrate complex of calcium (in English). R. K. Patnaik and S. Pani (College of Engineering, Sambulpur, Orissa, India). *J. Indian Chem. Soc.*, 38 (1961) 239.
The citrate complex of calcium has been studied by the pH titration method in the pH range 7.1–7.25. Curves have been drawn relating the pH and the volume of NaOH added to a mixture of citric acid and calcium perchlorate. The titration curves indicate the formation of a very stable 1 : 1 complex $CaCit^-$.
The equilibrium constant K is calculated at different pH values and the mean value is found to be $2.66 \cdot 10^3$. [R.S.Sa.]

1125 – Composition and stability of some metal-5-sulphosalicylate complexes. C. V. Banks and R. S. Singh (Institute for Atomic Research and Department of Chemistry, Iowa State University, Ames, Iowa, U.S.A.). *J. Inorg. and Nuclear Chem.*, 15 (1960) 125–132.
A potentiometric study of the 5-sulphosalicylate complexes of Al(III), U(VI), Ni(II), Co(II) and Mn(II) is made. For the Al(III) and U(VI)-5-sulphosalicylate complexes, both potentiometric and

spectrophotometric studies were made. Formation of 1 : 1, 1 : 2 and 1 : 3 complexes, at pH values of 3.8, 5.5 and 8.5 respectively, has been observed for Al(III), and of 1 : 1, 1 : 2 complexes, at pH values of 4.5 and 7.5 respectively, for U(VI). For the Be(II)- and Cu(II)-5-sulphosalicylate complexes the values of the stability constants have been recalculated. Using the potentiometric method, the step-wise stability constants of some metal complexes of the 5-sulphosalicylic acid have been calculated. [Su.Mo.Ce.]

1126 – Potentiometric determination of carbon in non-ferrous metals (in German). W. Fischer and H. Bastius (Forschungsinstitut für Nichteisen-Metalle, Freiberg-Sachs, Deutschland). *Metall*, 14 (1960) 429–434.
Carbon traces in Cu, Ti, titatium alloys, V, Ni and Mo can be determined by a modification of the procedure described by Fischer and Schmidt (*Anal. Abstr.*, 4 (1957) 432). A great excess of Cu must be added in the case of Ti and Ti alloys. [Gio.Ser.]

1127 – Potentiometric determination of titanium(III) with vanadium(IV). B. V. S. R. Murty and G. Gopala Rao (Andhra University, Waltair, India). *Talanta*, 8 (1961) 457–551.
The best conditions have been investigated for the accurate potentiometric determination of titanium(III) with standard 0.05 *N* vanadium(IV) sulphate solution. It was found that the titration can be carried out in a 1.0 *N* hydrochloric acid medium and carbon dioxide atmosphere at room temperature, in the presence of oxalic acid, within concentration limits of 0.06–0.1 *M*. A bright platinum-wire can be used as an indicator electrode and a saturated calomel electrode as comparison electrode. The vanadium(IV) sulphate was prepared by reducing ammonium vanadate with sulphur dioxide and removing the excess of sulphur dioxide by passing carbon dioxide. The solution was standardized by titration with standard potassium permanganate at 50°–60°. The visual titration was not successful. The recommended procedure gives accurate results within ± 0.2%. [J.Inc.]

1128 – Potentiometric study of zirconium nitrate and zirconium fluoride systems. A. J. Moffat (Phillips Petroleum Co., Atomic Energy Division, Idaho Falls, U.S.A.) *Nuclear Sci. Abstr.*, 15 (1961) 27, *Abstr. No.* 197. . [Red.]

1129 – Combined potentiometric determination of serum bicarbonate and chloride. M. Rockenmacher (Clinical Laboratory, Department of Pathology, Los Angeles County Harbor General Hospital, Torrance, Calif., U. S. A.). *Am. J. Clin. Pathhol.*, 33 (1960) 349–354.
By this titrimetric technique, only 0.2 ml of serum is required for the determination. The results obtained by this method compare favorably with those obtained by the Van Slyke and Whitehorn techniques. [Gio.Ser.]

1130 – The influence of pH and mixing of solutions on the electric tension of galena electrodes (in Polish). J. Czubak-Pawlikowska (Department of Surface Phenomena, Institute of Physical Chemistry, Polish Academy of Sciences, Kraków, Poland). *Roczniki Chem.*, 35 (1961) 285–290.
The electric tension of the galena electrode was investigated in acetate and ammonia buffers in the pH range 3–11, and in NaOH solutions in the pH range 10–12. The electric tension of the electrode decreases with increase of pH. It depends on the time from the beginning of the experiments, the greatest changes being observed in weakly alkaline solutions. Excluding the first moment, the electric tension of the electrode in a mixed solution is more positive, but these changes decrease with time, and after 24 h mixing has no influence. These phenomena indicate that the established electric tension results from surface reactions, which cover the electrode with a film of reaction products. [Ad.Hu.]

1131 – Equilibrium electric tensions of metals in fused electrolytes (in Russian). M. V. Smirnov and L. D. Yushina (Ural Department of the Academy of Sciences, U.S.S.R.). *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk.*, (1959) 251–258.
The equilibrium electric tension of thorium has been determined in chloride melts containing initially 0.14–78% $ThCl_4$ in the interval 680°–825°. The molten mixtures of sodium and potassium chlorides with $ThCl_2$ behave as ideal mixtures at all $ThCl_2$ concentrations. The temperature and concentration dependence of the thorium equilibrium electric tension have been determined. The redox electric tension and the equilibrium constant of the reaction $Th^{4+}(melt) + Th = 2Th^{2+}(melt)$ have been determined. [Ot.So.]

1132 – Degradation of ammonium paramolybdate by alkali (in English). K. V. R. Chari, D. V. S. Jain and R. P. Mitra (University of Delhi, India). *J. Sci. Ind. Research (India)*, 20 B (1961) 130.

Potentiometric and conductometric titrations of ammonium paramolybdate with KOH show that the alkali first degrades the paramolybdate into orthomolybdate between pH 5 and 7 and replacement of NH_4 by K ions takes place at a higher pH. Degradation is the only action of NH_4OH on paramolybdate. [R.S.Sa.]

1133 – Potentiometric determination of phosphate using a lead electrode (in Polish). J. Woźniak (Department of Food Investigation, State Institute of Hygiene, Warsaw, Poland). *Roczniki Państwowego Zakladu Hig.*, 12 (1961) 33–39.
A potentiometric method of phosphorus determination has been developed. It is based on the titration of 50 ml 0.03 *M* lead acetate with 0.2 *M* Na_2HPO_4, using a lead electrode as an indicator electrode. Best results were obtained when the pH was about 8.8, but it can decrease to 4.5. The presence of Ca, Mg, SO_4 and Cl does not interfere if these components are present in amounts of 7, 0.2, 3, 0.67 respectively, compared to phosphorus. [Ad.Hu.]

1134 – Gravimetric and titrimetric determination of bismuth using ammonium salts of benzene and naphthalene selenoic acids (in English). V. S. Sotnikov and I. P. Alimarin (Lomonosov Moscow University, Moscow, U.S.S.R.). *Talanta*, 8 (1961) 588–592.
Two new reagents have been proposed for the determination of bismuth. These are ammonium benzene selenoate, $C_6H_5SeO_2NH_4$ and ammonium naphthalene selenoate, $C_{10}H_7SeO_2NH_4$. The determination is possible in the presence of many other metal ions.
With bismuth ions the reagents form crystalline precipitates, $Bi(C_6H_5SeO_2)_3$ and $Bi(C_{10}H_7SeO_2)_3$ respectively, in acid solutions. The bismuth can be determined after drying at 110–120° by weighing, or titrimetrically after dissolving the $Bi(C_6H_5SeO_2)_3$ precipitate in a mixture of hydrochloric and tartaric acids. The titrimetric determination is based on the following reaction:

$$2\ C_6H_5SeO_2H + 6\ KI + 6\ HCl = (C_6H_5Se)_2 + 3\ I_2 + 6\ KCl + 4\ H_2O$$

The liberated iodine can be titrated with sodium thiosulphate, potentiometrically or amperometrically using a rotating platinum electrode. Lead does not interfere if the quantity of lead is not more than 10% of the bismuth. [J.Inc.]

1135 – Possible galvanic method for monitoring activity of oxygen in a hot-trapped sodium coolant circuit. G. W. Horsley (U.K.A.E.A. Research Group, Harwell, Berks., Gt. Britain). *Nuclear Sci. Abstr.*, 15 (1961) 1387, *Abstr. No.* 10828. [Red.]

1136 – Membrane electrode cell for determination of dissolved O_2. R. W. Henkons (General Electric Co, Hanford Atomic Products Operation, Richland, Wash., U.S.A.). *Nuclear Sci. Abstr.*, 15 (1961) 18, *Abstr., No.* 126. [Red.]

1137 – Determination of chromium and aluminium in the presence of each other with EDTA (in Italian). A. Furlani Donda (Institute of General Chemistry, University of Rome, Italy). *Gazz. chim. ital.*, 90 (1960) 1380–1393.
Two methods are proposed for the determination of Cr and Al in the presence of each other. (i) The sum Al + Cr is determined potentiometrically using an excess of EDTA and back titration with Zn^{2+} at pH 5 in the presence of ferro- and ferricyanide (a platinum electrode *vs.* S.C.E.). (ii) Cr alone can be determined colorimetrically, or Al is masked by NaF and another back titration with Zn^{2+} is performed in the EDTA released from the Al-complex. [Fr.Pan.]

1138 – An electrometric study of chromium salicylate complex ion (in English). J. P. Tandon and R. C. Mahrotra (University of Gorakhpur, India). *J. Indian Chem. Soc.*, 38 (1961) 169.
The reaction between trivalent chromium and salicylate ions has been studied by means of electrometric titrations. The measurements of pH have been carried out in freshly mixed solutions as well as after ageing at room temperature or by heating. A suitable reaction mechanism has been proposed for the titration curves obtained, which has been further verified by isolating and analysing the products formed by mixing the reactants in different partial molar ratios. The physicochemical study gives evidence for mono- and di-salicylate complexes whereas the disalicylate is the only products of the precipitation reactions. [R.S.Sa.]

1139 – An indirect potentiometric method for estimation of micro amounts of selenium (in German). H. Hahn and H. Bartels (Chemisches Institut, Abteilung für anorganische Chemie, Universität Würzburg, Deutschland). *Mikrochim. Acta*, (1961) 250–261.
First the authors demonstrate the accuracy of their method of titrating potentiometrically micro amounts of silver (0.5–250 μg) by KI in a volume of 5 ml. At this concentration it is necessary to

use red light. Afterwards, the procedure is given for the reduction of SeO_3^{2-} by hydrazine sulfate to Se^{2-} in the presence of an excess of Ag^+, which involves the precipitation of Ag_2Se. Then the excess of the reducing agent is destroyed by heating the solution to 105° because its presence disturbs the titration of Ag^+ with I^-. The error is 1–2%. [H.L.Ki.]

1140 – Chromometric determination of hexavalent molybdenum in the presence of thiocyanates (in Russian). A. I. Busev and Gyn Li. *Vestnik Moskov. Univ., Ser. Khim.*, 11 (1960) 73–75.
By using a Pt indicator electrode, the potentiometric titration of Mo^{6+} with $CrCl_2$ in the presence of KSCN in HCl solution has been studied. 80 ml of soln. containing 9.6 mg of Mo in 6 *N* HCl are gassed with CO_2 for 25 min. After the addition of 1 g KSCN, CO_2 is passed for another 5 min and the titration is carried out. The results obtained at room temperature are given. [Gio.Ser.]

1141 – Propriétés chimiques de quelques composés de l'uranium dans les chlorures alcalins fondus (en français). R. Molina (Laboratoire de Chimie Analytique, E.P.C.I., Paris 5e, France). *Bull. soc. chim. France*, (1961) 1184–1190.
L'auteur continue l'étude qu'il à déja entreprise (R. Molina, *Bull. soc. chim. France*, (1960) 901; (1961) 1001) pour établir les diagrammes tension électrique normale apparente E''_0/pO^{2-} dans l'eutectique fondu LiCl–KCl. Il s'intéresse ici aux systèmes de l'uranium. On établit tout d'abord par spectrophotométrie que les espèces U^{3+}, U^{4+}, $UO_2\downarrow$, UO_2^{2+} et $UO_3\downarrow$ existent dans le mileu. Puis à l'aide des réactions déjà décrites (formation de complexes de O^{2-} avec $NaPO_3$, $Na_2S_2O_7$, HCl, NH_4Cl et V_2O_5 ou oxydation de O^{2-} par Cu^{2+}, Cl_2 ou $S_2O_8^{2-}$) il étudie les moyens de dissoudre les deux précipités $UO_2\downarrow$ et $UO_3\downarrow$ Les produits de solubilité de ces deux corps étant respectivement de 9 et 4.6 et différents publications ayant indiqué les tensions électriques normales de $U\downarrow/U(III)$, de $U(III)/U(IV)$ et de $U(IV)/U(VI)$ (soit respectivement —2.215 V, —1.144 V et —.286 V), par rapport à l'électrode de comparaison $Pt\downarrow/Pt$ (II) (1 *M*) il est possible de tracer le diagramme E''_0/pO^{2-}. D'autre part ce même diagramme est connu qualitativement pour les systèmes du soufre. La superposition des deux diagrammes permet à la fois de preciser leur position dans l'échelle des tensions électriques et d'expliquer quelques reactions entre les composés oxygénés du soufre et de l'uranium. [J.Des.]

1142 – Studies on uranium(VI) compounds with phthalic acid (in English). Jit Singh and K. Prasad (Atomic Energy Establishment, Bombay, India). *J. Sci. Ind. Research (India)*, 20 B (1961) 104.
Potentiometric and spectrophotometric studies on the uranium (VI)–phthalic acid system indicate the formation of a soluble uranyl phthalate complex and an insoluble ammonium salt. Based on X-ray and chemical analysis, and substantiated by potentiometric data, the structure for the insoluble compound has been discussed and a dimeric molecular formula $(NH_4)_2C_6H_4(COO)_2U_2O_5$ has been assigned to it. [R.S.Sa.]

1143 – Potentiometric and high-frequency titration of trace amounts of chlorides and mercaptans (in English). N. van Meurs (Koninklijke/Shell Laboratorium, Shell International Research Maatschappij N. V., Amsterdam, The Netherlands). *J. Electroanal. Chem.*, 2 (1961) 17–24.
A study of the potentiometric and high-frequency titration of trace amounts of chlorides and mercaptans in aqueous and nonaqueous solutions is described. It is shown that the two techniques, while being simpler than the amperometric methods hitherto used, give similar results with respect to sensitivity and accuracy. By means of potentiometry, mixtures of chlorides and mercaptans can be analysed and this method can also be used for the determination of traces of chloride in concentrated aqueous salt solutions. [Author]

1144 – Precision null-point potentiometry. Direct microdetermination of iodide in solutions with high chloride concentrations. H. V. Malmstadt and J. D. Winefordner (Department of Chemistry and Chemical Engineering, University of Illinois, Urbana, Ill., U.S.A.). *Anal. Chim. Acta*, 24 (1961) 91–96.
The null-point potentiometric method has been applied to the determination of micro amounts of iodide in the presence of large concentrations of chloride. Silver–silver iodide electrodes have been used because they are sensitive to iodide concentrations and can readily be prepared. The titration can be performed directly and rapidly, the complete analysis time being about 3 minutes. When the sodium chloride to iodide weight ratio was as high as 200,000 : 1, relative errors of about 0.5% at 100 p.p.m. and about 5% at 10 p.p.m. iodide were observed. The measured samples contained 1–20 μg of iodide in 20 ml of solution. [P.Me.]

1145 – Potentiometric finish in the Schöniger halogen method. D. G. Newman and C. Tom-

linson (Microanalytical Laboratory, Department of Organic Chemistry, Liverpool University, England). *Mikrochim. Acta*, (1961) 73–74.
In order that the liquid in the flask may be sufficiently deep for insertion of the electrode system (Ag — Hg_2SO_4/Hg) and the magnetic stirrer at a total volume of 50 ml, the form of the flask is modified. Also, as incomplete destruction of the perhydroxy and high salt concentrations make the results somewhat indeterminate, the chemical procedure is somewhat altered. The standard deviation is about 0.25%. [H.L.Ki.]

1146 – Estimation of the radius of some ions adsorbed by silver iodide surfaces (in German). E. Pungor and I. Konkoly Thege (Institute of Inorganic Analytical Chemistry, Eötvös University, Budapest, Hungary). *Ann. Univ. Sci. Budapest. Rolando Eötvös nominatae, Sect. Chim.*, 2 (1960) 31–33.
Using end-point indication by potentiometry and by coloured indicators, it was found that in the presence of other halide ions, pseudohalides, sulphate and phosphate, it was not possible to determine iodide precisely using *p*-ethoxy chrysoidine as an indicator as a high consumption of silver nitrate appears in the titration results. The phenomenon may be interpreted by the Schulek-Pungor theory of adsorption indicators. On the basis of the phenomenon, the ion radii of chloride, bromide, thiocyanate, sulphate and phosphate ions were calculated by the authors. With the exception of the last two ions, the others proved to be adsorbed without water molecules. In the case of sulphate and phosphate, the results of calculations indicated adsorption, together with eight molecules of water. [E.Pun.]

1147 – Recent achievements in the field of interhaloid complexes (in German). E. Pungor, E. Schulek and K. Burger (Institute of Inorganic and Analytical Chemistry, Eötvös University, Budapest, Hungary). *Ann. Univ. Sci. Budapest. Rolando Eötvös nominatae, Sect. Chim.*, 2 (1960) 93–97.
The coordination numbers and stability constants of complexes in the presence of halide acids may be calculated using redox electric tension measurements of interhaloids. At the same time, the hydrolysis constants of interhaloids and halogens were obtainable from measurements of pH values. By following the reaction of cyanogen bromide with iodide by photometry, a basis was obtained from which quantitative conclusions could be drawn with respect to the formation of the various complexes of cyanogen bromide. The authors emphasized that the notation applied in this context to interhaloids and cyanogen halides should be avoided in the future. Instead, the presentation of the compound in question as a complex is suggested. [E.Pun.]

1148 – On the oxidation tension of permanganate (in Russian). I. P. Alekseeva, V. M. Pesockaya and B. V. Ptitsin (Technological Institute of the Food Industry, Leningrad, U.S.S.R.). *Zhur. Obscheĭ Khim.*, 30 (1960) 2104–2108.
The dependence of the oxidation electric tension of a 0.01 *M* $KMnO_4$ solution in $HClO_4$, HNO_3, H_2SO_4 and CH_3COOH solutions has been investigated potentiometrically using a bright platinum and a saturated calomel electrode. The pH was measured by a glass electrode. Agitation had no effect on the magnitude and rate of stabilisation of the electric tension. Data for the pH dependence of the oxidation electric tension are tabulated, and it is shown that at low pH values the nature of the acid influences the potential value. [Ot.So.]

1149 – Stability constants of some metal complexes of ortho-aminophenols (note) D. D. Perrin (Department of Medical Chemistry, The Australian National University, Canberra, Australia). *J. Chem. Soc.*, (1961) 2244–2246.
Potentiometric measurements show that the values for the stability constants of Fe(II) previously reported by Sims are definitely too high, as a result of oxidation to the ferric state. The new values (about 3.6 for *o*-aminophenol and 3.8 for 3-hydroxyanthranilic acid) now fall into their predicted places in the series proposed by Irving and Williams for the stability constants of metal complexes. [L.Gi.]

1150 – Studies on some less familiar ferrocyanogen complexes. XI. Composition of chromic ferrocyanide complex by electrometric methods (in English). Wabid U. Malik (Aligarh Muslim University, Aligarh, India). *J. Sci. Ind. Research (India)*, 20 B (1961) 213.
Conductometric pH and e.m.f. measurements of chromic chloride and $K_4Fe(CN)_6$ mixtures for different concentrations have been carried out. Variations in pH and e.m.f. when plotted against the concentrations of either of the reactants give evidence for the existence of $KCrFe(CN)_6$. $K_4Fe(CN)_6$ and $KCrFe(CN)_6$ adsorption complexes. Conductometric titrations do not provide conclusive evidence. The chromic ferrocyanide complex is not reducible at the dropping mercury electrode. The polarographic method offers a method for determining its composition. The minimum current values at +1.5 V when plotted against the volume of the chromic chloride give a combining ratio of 1 : 1 for $CrCl_3$ and $K_4Fe(CN)_6$. [R.S.Sa.]

1151 – The influence of acids and salts on the use of chromous chloride as a reducing titrant. Wahid U. Malik and K. M. Abubacker (Department of Chemistry, Muslim University, Aligarh, India). *Anal. Chim. Acta*, 23 (1960) 518–523.

The influence of different concentrations of acids and salts on the titration of copper sulphate with chromous chloride solution is studied. As chromous chloride solutions must be standardized regularly, the authors developed a quick and accurate potassium permanganate potentiometric titration. Potentiometry was also used for the study of copper sulphate titration with chromous chloride solution. The titration curves showed two breaks, the second of which was usually pronounced, but sharp breaks in the first stage were only obtained in the presence of hydrochloric acid and potassium chloride, separately or together. Better results can, however, be achieved when sufficient hydrogen ions are also added to prevent hydrolysis. Titrations at high temperatures did not appear to be preferable. [P.Me.]

1152 – The determination of cobalt in heat resistant alloys. H. Kirtchik and E. H. Swearingen (Flight Propulsion Laboratory Dept., General Electric Co., Evendale 15, Ohio, U.S.A.). *Analyst*, 86 (1961) 188–195.

In this method the Co is precipitated by phenylthiohydantoic and thioglycollic acids, the traces of Fe and Ni accompanying the Co precipitate offering no hindrance to the subsequent potentiometric titration of Co with $K_3Fe(CN)_6$ in the presence of ethylenediamine. Dissolve 50–300 mg of sample containing 6–50 mg Co in aqua regia. Add 5 ml of 85% H_3PO_4, 20 ml of 50% H_2SO_4 and 5 ml of 70% $HClO_4$. Evaporate until rest of $HClO_4$ has been removed. Cool, add 25 ml H_2O and boil to dissolve salts. Dilute to 150 ml with H_2O, add 10 g ammonium citrate and stir. Add 0.880 NH_3 to pH 8, then 10 ml excess. Dilute to 250 ml, cool to 35° and add 4 ml thioglycollic acid. Stir, leave 2–3 min, add ashless filter pulp, then with stirring 35 ml of 4% w/v phenylthiohydantoic acid in EtOH. Heat to boiling point, stir vigorously and simmer 5 min. Add further 5 ml phenylthiohydantoic acid, simmer further 5 min then filter through Whatman No. 42 paper. Wash well with hot buffer solution containing 0.5% ammonium citrate, 0.5% v/v 0.880 NH_3, 1% of alcoholic phenylhydantoic acid reagent. Decompose precipitate by solution in 35 ml HNO_3 plus 12 ml of 70% $HClO_4$, boiling vigorously until fuming. Add this to a mixture of 100 ml ammonium citrate buffer, 80 ml 0.880 NH_3 and a known excess of 1.100% $K_3Fe(CN)_6$. Stir well and back titrate the excess of $K_3Fe(CN)_6$ with $Co(NO_3)_2$ solution containing 0.200% Co. The electrode assembly is Pt indicator and saturated calomel comparison and a pH-meter is used, the end-point being taken as that 0.05 ml portion which produces the largest change of electrical tension. For samples containing 3% Co the accuracy is 2–4% of that present. [P.O.Ka.]

1153 – Determination of cobalt by potentiometric titration with iron(III)-salts in the presence of 1.1 *M* phenanthroline (in German). F. Vydra and R. Přibil (Institute of Geochemistry and Inorganic Raw Materials, Czechoslovak Academy of Sciences, Prague, Czechoslovakia). *Collection Czechoslov. Chem. Communs.*, 26 (1961) 2169–2173.

For the determination of cobalt in pure solutions the sample solution is mixed with 10 ml buffer (monochloroacetic acid + ammonia, pH about 3) and 0.1 *M* phenanthroline. The mixture is diluted to 50 ml and titrated by a 0.01–0.0001 *M* $FeCl_3$ volumetric solution using a platinum and a saturated calomel electrode.

For the analysis of alloys, the sample is dissolved in a suitable acid (acid mixture) and evaporated. Chromium must be present as Cr(III). After dissolving in water, the solution is made about 2 *N* in HCl and shaken with mercury. After removal of the mercury the solution is brought to pH 3 by ammonia, and the above procedure is followed. Metals which react with phenanthroline interfere by decreasing its concentration. Under optimum conditions the method is specific for cobalt. [Ot.So.]

1154 – Thermodynamics of ion association. VII. Some transition metal oxalates. A. McAuley and G. H. Nancollas (The University, Glasgow, Great Britain). *J. Chem. Soc.*, (1961) 2215–2221.

The various thermodynamic quantities (*e.g.* constants ΔG, ΔH, ΔS, ΔC_p) relative to the association reaction $M^{2+} + C_2O_4^{2-} \rightleftharpoons MC_2O_4$ (with M = Ni, Co, Mn) have been determined and are discussed. The high precision potentiometric method of Nair and Nancollas (*J. Chem. Soc.*, (1958) 4144) was used. [L.Gi.]

1155 – Determination of compositions of basic salts of nickel from potentiometric studies (in English). R. M. Mallya and A. R. Vasudev Murthy (Indian Institute of Science, Bangalore, India). *J. Sci. Ind. Research (India)*, 20 B (1961) 62.

The precipitation of basic nickel salts from aqueous solutions of nickel sulphate and chloride has been followed potentiometrically using the glass electrode. By making allowance for the initial acidity of the nickel salt solution the compositions of the precipitates were found to be $0.8Ni(OH)_2$,

$0.2NiSO_4$ and $0.8Ni(OH)_2$, $0.2NiCl_2$ for the basic sulphate and chloride. This is in support of the composition $4Ni(OH)_2.NiSO_4$ for which considerable evidence has been obtained by previous workers. [R.S.Sa.]

1156 – The use of ruthenium tetroxide as a catalyst in redox titrations. C. J. Keattch (International Nickel Co. Ltd., Development and Research Department, London, England). *Talanta*, 8 (1961) 620–623.
In view of the chemical similarity between osmium and ruthenium tetroxides, ruthenium tetroxide was tested as a catalyst in the titration of arsenious oxide with ceric sulphate in acidic media, as well as of sulphite with ferricyanide in alkaline media. The end-points of the redox titrations were determined by both visual and potentiometric methods. In the latter case a platinum/saturated calomel electrode system was used. It was found that the osmium tetroxide is a stronger catalyst than the ruthenium analogue, and this may possibly be explained by assigning different structures to the two compounds. In the titration of arsenious oxide with ceric sulphate, ruthenium tetroxide can be used as a catalyst only if a potentiometric end-point is employed. In the determination of sulphite with ferricyanide the reaction is catalysed equally well by ruthenium or osmium tetroxide. [J.Inc.]

1157 – The influence of counter-ion radius on association in aqueous polymethacrylate solutions (in Italian). V. Crescenzi, A. De Chirico and A. Ripamonti (Inst. of General Chem., University of Bari, Italy). *Ricerca sci.*, 29 (1959) 1424–29.
Over a wide range of neutralization of polymethacrylic acid with rubidium, sodium or lithium hydroxide, the activity coefficients were determined for the alkaline ions by means of membrane potential measurements. In every case the activity coefficients of the counter-ions decreased from Rb to Li. [Fr.Pan.]

1158 – Behaviour of sodium diethyldithiocarbamate in non-aqueous solvents (in English). K. P. Soni and A. M. Trivedi (M. G. Science Institute, Ahemdabad, India). *J. Indian Chem. Soc.*, 38 (1961) 65.
A simple potentiometric method has been suggested for estimating dithiocarbamates by titration (dissolved in acetic acid) against perchloric acid in *p*-dioxane, when both the groups are estimated. The titration of the substance in acetic anhydride reveals the first break, while in acetic acid as solvent it shows an overall jump, corresponding to the utilisation of two equivalents of $HClO_4$ in *p*-dioxane. This procedure gives accurate results. The presence of basic impurities interferes with the estimation. [R.S.Sa.]

1159 – Electrochemistry in acetonitrile (in French). J. P. Billon (Laboratoire de Chimie Analytique de l'Ecole Supérieure de Physique et de Chimie Industrielles, Paris, et Société Rhône-Poulenc, Laboratoires de Recherches de Vitry, Seine, France). *J. Electroanal. Chem.*, 1 (1959/1960) 486–501.
We have studied the electrochemical properties of acetonitrile using a polished platinum electrode. By means of the intensity–electric tension curves it is possible to define the range in which the oxydo-reduction reactions can take place at a platinum electrode in this solvent. We have prepared H^+ ions in sufficient yield by oxidation of the solvent. In the reduction the electrochemical reactions which limit the range of oxide reduction depend on the electrolyte used; we observed a great difference in behaviour according to whether the cation of the electrolyte was Li^+, Na^+ or $(C_4H_9)_4N^+$. [Author]

1160 – Ionization of ethylenediaminetetraacetic acid and its acid salts. D. C. Olson and D. W. Margerum (Department of Chemistry, Purdue University, Lafayette, Ind., U.S.A.). *J. Am. Chem. Soc.*, 82 (1960) 5602–5605.
By means of crystallization of EDTA from 6 *M* HCl the authors have prepared the fully protonated salt H_6YCl_2. Spectral measurements were employed to determine the dissociation constants for H_6Y^{2+} and H_5Y^+; the values at 25° and $\mu = 2.0$ are $K_{H_6Y^{2+}} = 0.55$ and $K_{H_5Y^+} = 0.11$. A titrimetric method was used to evaluate the K_1 dissociation constant (for H_4Y); its value at 25° and $\mu = 2.0$ is $2.0 \cdot 10^{-3}$. These data and other EDTA constants support the betaine structure for H_4Y. The data indicate that the previously proposed tetraacetic acid structure of H_4Y is not valid in solution. [R.W.Mur.]

1161 – Potassium periodate as a volumetric reagent. Determination of organic derivatives of hydrazine (in English). Balvant Singh, S. S. Sahota, and Mohindra Pal Gupta (Panjab University, Chandigarh, India). *J. Indian Chem. Soc.*, 38 (1961) 189.
Potassium periodate in the presence of HCl, has been used as an oxidant for the potentiometric determination of nitroaminoguanidine, β-formylphenylhydrazine, β-acetylphenylhydrazine, adipic

diphenylhydrazide, β-propionyl-phenylhydrazine, 2:4-dinitrophenylhydrazine, *o*- and *p*-chlorobenzylidene semicarbazones, cinnamylidene semicarbazone, hydrazine sulphate, semicarbazide hydrochloride, benzylidene semicarbazone, 4-phenylsemicarbazide, benzalazine, and 4-hydroxy-3-methoxybenzylidene semicarbazone. In potentiometric titrations, the platinum electrode has been used as an oxidation–reduction electrode, in conjunction with a saturated calomel electrode. At the equivalence-point a sharp jump in tension is observed in each titration. In these compounds each hydrazine group is quantitatively oxidised to nitrogen with potassium periodate by a four-electron change. [R.S.Sa.]

1162 – Dosage potentiométrique des mélanges d'hydrazine et de diméthylhydrazine asymétrique. G. Pannetier et P. Mignotte (Laboratoire de Chimie générale du Centre d'Orsay de la Faculté des Sciences de Paris, France). *Bull. soc. chim. France*, (1961) 1380–1381.
Les auteurs désirent doser séparément et en présence l'une de l'autre l'hydrazine et la diméthylhydrazine. Pour celà, ils utilisent tout d'abord un titrage potentiométrique à l'électrode de verre (détermination de la basicité totale; à une molécule d'acide correspond une molécule d'hydrazine ou une molécule de diméthylhydrazine). Ensuite, en milieu chlorhydrique concentré, on fait un titrage d'oxydoréduction par l'iodate. La réaction est suivie par potentiométrie à l'électrode de platine. A une mole d'iodate correspond une mole d'hydrazine ou une demie mole de diméthylhydrazine. Si, en outre, le poids exact de l'échantillon est connu, il est possible, par différence, de calculer la quantité d'eau contenue dans le mélange. Un mode opératoire indique la manière de procéder pour effectuer les deux déterminations expérimentales avec une seule prise d'essai. Les auteurs estiment la précision à trois pour cent pour chacune des deux hydrazines et à 0.5 pour cent si seule la diméthylhydrazine est présente. [J.Des.]

1163 – The determination of thiomalic acid. A. I. Busev and Chzhan Fan' (Department of Chemistry, Lomonosov University, Moscow, U.S.S.R.). *Talanta*, 8 (1961) 470–472.
A method has been developed for the determination of thiomalic acid. The procedure is to oxidize the acid with an excess of iodine in a strong alkaline medium and to back titrate the excess, after acidification, with thiosulphate solution. Thiomalic acid may also be titrated potentiometrically with standard sodium hydroxide solution using a glass electrode. [J.Inc.]

1164 – Transmutations in water-free benzoyl bromide (in German). V. Gutmann and K. Utvary (Institut für anorganische und allgemeine Chemie, Technische Hochschule, Wien, Österreich). *Monatsh. Chem.*, 90 (1959) 751–761.
Many metal bromides are soluble in benzoyl bromide. By potentiometric titration with tetrabutylammonium bromide it was found that the bromides can accept extra Br^- ions (one in the case of $SnBr_4$ and two for $TiBr_4$) forming a complex. $SnBr_4$ and $TiBr_4$ show no intermediate formation of $SnBr_5^-$ or $TiBr_5^-$.
From measurements of the electric tensions in half neutralised solutions, it follows that the "acid" properties of the bromides in a group of the periodic system increase with increasing cationic radius, (*e.g.* $AlBr_3 < GaBr_3 < InBr_3$), and in a period decrease with increasing atomic number. On standing, the originally colourless solutions become coloured. This is accompanied by a decrease in the amount of tetraalkyl-ammonium bromide needed for neutralisation. This effect is attributed to the formation of solvates. [C.I.Moo.]

1165 – Studies on legume starches. IV. Separation and determination of amylose and amylopectin. II. Iodine coloration and potentiometric titration. Sin'itiro Kawamura and Minoru Tada (Faculty of Agriculture, Kagawa University, Miki-cho, Kagawa-ken, Japan), *J. Agr. Chem. Soc. Japan*, 33 (1959) 296–300.
Amylose and amylopectin are separated from legume and potato starch by extracting with 1% NaOH and precipitating with butanol.
By colorimetry and potentiometric titration it is possible to determine the amount of the different compounds. [Gio.Ser.]

1166 – Typical contaminations accompanying quinoline bases (in English). B. Malanowska and S. Malanowski (Institute of General Chemistry, Warsaw, Poland). *Bull. acad. polon. sci.*, 9 (1961) 123–126.
On the basis of solubility determinations of indole, 2-methyl-naphthalene, phenol and 2,4- xylenol in aqueous quinoline sulphate solution containing excess of sulphuric acid, the best conditions for the removal of these contaminations were investigated. Taking into account the decrease of solubility with increase of pH, and the increase of extractibility of quinoline at higher pH, the optimum conditions were established on the basis of the curve of potentiometric titration of quinoline. Highest efficiency of extraction of contaminants was found at pH = 3.5. [Ad.Hu.]

1167 – Inductive effects on the acid dissociation constants of mercaptans. M. M. Kreevoy and others (School of Chemistry, University of Minnesota, Minneapolis 14, Minn., U.S.A.). *J. Am. Chem. Soc.*, 82 (1960) 4899–4902.
The authors have measured the acid dissociation constants of a number of mercaptans using pH titrations, spectrophotometric data, and gas solubility data. The results are correlated in terms of inductive effects and the Taft inductive parameter σ^*. [R.W.Mur.]

1168 – The determination of sulphydryl groups in reduced hair keratin. Herman H. Stein and Julia Guarnaccio (Research Laboratories, The Toni Company, Chicago, Ill., U.S.A.). *Anal. Chim. Acta*, 23 (1960) 89–97.
A method has been proposed for the determination of sulphydryl groups in reduced hair keratin. The sample of human hair is first immersed in a basic thioglycolate solution, this treatment being known to convert the disulfide bond in keratin to thiol groups. The excess thioglycolate is removed by washings in hot glacial acetic acid, iodoacetamide is added to the sample and the iodide ions generated in the reaction between the sulphydryl group and iodoacetamide are titrated potentiometrically with silver nitrate. The standard error of the method is of the order of 0.010 mequivs mercaptan/g hair. [P.Me.]

1169 – Etude de la dissociation acide de quelques sulfonamides (in French). G. Dauphin et A. Kergomard (Laboratoire de Chimie Systématique, Faculté des Sciences, Clermont-Ferrand, France). *Bull. soc. chim. France*, (1961) 486–492.
Les auteurs se proposent de vérifier la loi de Hammett pour les Kp de quelques 70 sulfonamides et de différentes sulfonimides. Cette loi s'exprime par $pK = pK_0 - \varrho\sigma$, ou, dans le cas de deux substituants $pK = pK_0 - \varrho_1\sigma_1 - \varrho_2\sigma_2$. On opère par titrage potentiométrique à l'électrode de verre dans des mélanges hydroalcoolique à 0; 7.6; 15.4; 23.4; 31.6 et 40% d'alcool (en poids). A chaque valeur de pH obtenue par adjonction de soude on fait correspondre par le calcul, une valeur de pK. Le pK adopté est la moyenne des valeurs précédentes.
Pour chaque série de corps considérés, sont indiquées les constantes de réaction ϱ et de corrélation σ ainsi que la déviation standard et l'erreur absolue sur ϱ. Ces déterminations se font–à partir des résultats expérimentaux et des coefficients σ connus–par la méthode des moindres carrés. Les σ obtenus, ici, pour (p)SO_2NH_2 et (M)SO_2NH_2 ne sont pas en accord avec celles données par la littérature.
La loi de Hammett (généralisée s'il y a lieu) est vérifiée dans les cas décrits. Les préparations des corps utilisés sont indiquées. [J.Des.]

1170 – Determination of sulphonylamides with alkyl nitrites by a potentiometric method. N. K. Mathur, S. P. Rao and O. P. Kachhawaha (Department of Chemistry, Jaswant College, Jodhpur, India). *Anal. Chim. Acta*, 24 (1961) 474–475.
Titration of a series of sulpha drugs was performed potentiometrically with a S.C.E. *vs.* a bright platinum indicator electrode, the equivalence point being indicated by a sudden change in the electric tension of the order of 80–120 mV. In addition to the classical method the "dead stop" technique with two platinum electrodes and a very small dE($\pm$15 mV) was also used for end-point detection. The method described has a maximum error of the order of 2%. [P.Me.]

1171 – The scope and mechanism of carbohydrate oxotriazole formation. VI. The apparent dissociation constant of triazole carboxylic acids. H. E. Khadem (Alexandria University, Chemical Department, Egypt). *J. Chem. Soc.*, (1961) 3146–3147.
The dissociation constants of 16 acids have been determined in the solvent methyl cellosolve–water (4 : 1 w/w). The results are briefly discussed. The triazole ring is a much stronger electron-attracting group than the benzene ring. [L.Gi.]

1172 – New methods for determination of pharmaceutical preparations using Reinecke salts (in Polish). A. Danek (Department of Inorganic and Analytical Chemistry, Academy of Medicine, Kraków, Poland). *Acta Polon. Pharm.*, 18 (1961) 229–234.
A potentiometric method for the determination of $[Cr(NH_3)_2(SCN)_4]^-$ has been developed. It consists of titration with standard $AgNO_3$ in acetone or acetone–water media, in which the organic salts of $[Cr(NH_3)_2(SCN)_4]^-$ are soluble, contrary to its silver salt. The electric tension changes were measured in a silver–saturated calomel electrode system with a KNO_3 salt bridge. This method was used for the determination of various preparations containing organic bases with a precision not greater than 0.76 mg for 10–20 mg samples. [Ad.Hu.]

See also abstracts nos. 955, 956, 984, 1187, 1191.

5. Conductometry

1173 – Physico-chemical aspects of conductometric acid–base titrations in non-aqueous media (in English). N. Van Meurs and E. A. M. F. Dahmen (Koninklijke/Shell Laboratorium, Shell Internationale Research Maatschappij N. V., Amsterdam, The Netherlands). *J. Electroanal. Chem.*, 1 (1959/1960) 458.

A theoretical and experimental study has been made of the conductometric titration of organic acids and bases in non-aqueous solvents.

The influence of the structure of bivalent acids and bases on the titration curves has been investigated and a possible explanation for the phenomena observed is put forward.

Special attention has been paid to some effects of temperature and its influence on the titration of bases. In this connection a semi-quantitative explanation is given of the temperature dependence of the conductance of solutions of acid sompounds. [Authors]

1174 – Conductometric titration of metal acetates in an aqueous medium. Franco Gaslini and Lucio Zion Nahum (Research Division, Cartiera Vita Mayer and Co., Milan, Italy). *Anal. Chim. Acta*, 24 (1961) 79–82.

When conductometric titration of a metal acetate is performed in an aqueous medium with a strong acid, the graph obtained shows at first a straight line, corresponding to the conductance variation due to the replacement of the anion CH_3COO^- by the titrant anion; the former combines with hydrogen ion of the titrant. When the equivalence point is reached, the conductance increases sharply as a consequence of the rapid increase of free hydrogen ions; the sharpness of the equivalence point angle depends on the values of the ionization constant, and of the anionic mobility of the titrant. Trichloroacetic acid seemed particularly suitable as titrant. Sixteen metal acetates have been titrated. From the values obtained by this method a standard deviation of 0.3% was calculated. [P.Me.]

1175 – Solutions of metals in amine solvents. IV. The effect of temperature on the conductance of lithium in methylamine. Armand J. Penson and H. Charles Evers (John Harrison Laboratory of Chemistry, University of Pennsylvania, Philadelphia, Penn., U.S.A.). *J. Am. Chem. Soc.*, 82 (1960) 4468.

The authors have measured the conductance of lithium in methylamine solvent over a range of temperatures from —78° to 20° in moderately dilute solutions. A maximum was observed in the specific conductance–temperature curves; this maximum shifted to higher temperatures with increasing concentration and was observed only for the more dilute solutions studied. Noting the qualitative similarity of these results to those for normal electrolytes in aqueous solutions, it has been concluded that the data provide evidence for mass action equilibria existing in these solutions. [R.W.Mur.]

1176 – Conductometric titration of sodium in liquid ammonia with phosphine, arsine, stibine and germanes. H. J. Emeleus and K. M. Mackay (University Chemistry Laboratory, Lensfield Road, Cambridge, Great Britain). *J. Chem. Soc.*, (1961) 2676–2680.

The stoichiometry of the reactions involved has been ascertained by conductometric titrations and by measurement of the quantity of hydrogen evolved. Disubstitution by sodium occurs in the early stages of the titration for arsine and stibine, in contrast with the behaviour of phosphine, where only monosubstitution is observed. In the case of monogermane, mono- and di-substitution occurs simultaneously in the early stages with subsequent reconversion of the disodium compound into the monosodium form. The reaction with di- and tri-germanes is more complex. It can be inferred from the results that the extent of formation of the disodium derivative increases with the electropositive character of the central atom. [L.Gi.]

1177 – A study of transfer and solvation phenomena. II. Silver perchlorate in water, water–ethanol and ethanol solvents. W. Ves Childs and E. S. Amis (Chemistry Department, University of Arkansas, Fayetteville, Ark., U.S.A.). *J. Inorg. and Nuclear Chem.*, 16 (1960) 114–123.

Transfer numbers (TN) and solvation of solutions of silver perchlorate have been determined. For solutions of $AgClO_4$ in water, the TN of silver ion decreases linearly with decreasing concentration of the salt. The value for TN at infinite dilution, obtained by extrapolation, is 0.488 ± 0.005. The number of moles of water carried per mole of cation decreases with increasing concentration of salt, as is to be expected.

For a 0.4 *M* $AgClO_4$ solution in water–ethanol, the variation of TN with the percentage of ethanol is reported. There is a linear decrease of the TN for silver ion with increasing percentages of ethanol. The rate of decrease is at first slow, then more rapid between 55–85% ethanol, when it

slows again. Solvation data for ethanol and for water solutions of $AgClO_4$ seem to indicate a preferential solvation of the silver ion by water and of the perchlorate ion by ethanol. [Su.Mo.Ce.]

1178 – Displacement titrations with high-frequency end point indication (in German). I. Krausz and Á. Endrói-Havas (Institute of Inorganic and Analytical Chemistry, Eötvös University, Budapest, Hungary). *Ann. Univ. Sci. Budapest. Rolando Eötvös nominatae, Sect. Chim.*, 2 (1960) 325–327.
High-frequency titration proved to be possible by displacement reactions in the case of the systems: sodium acetate trihydrate and sodium acetate–acetic acid, also, of sodium benzoate and of Seignette's salt. [E.Pun.]

1179 – Tables of resistivity of aqueous NaCl solution. G. F. Hewitt (U.K.A.E.A. Research Group, Atomic Energy Research Establishment, Harwell, Berks., Gt. Britain). *Nuclear Sci. Abstr.* 15 (1961) 650, *Abstr. No.* 5029. [Red.]

1180 – High frequency titration: estimation of barium, calcium and magnesium ions and determination of the hardness of water (in English). S. N. Mukherjee and P. K. Bhattacharjee (Physical Chemistry Laboratory, Jadavpur University, Calcutta, India). *Sci. and Culture (Calcutta)* 25 (1959) 153.
By using the technique described previously, barium is titrated with sulphate using the break in the capacity concentration curve as end-point. For greatest accuracy the titration is conducted in 50% ethanol. Using a frequency of 475 Mc/sec as in the apparatus described, the useful range of concentration is $2–8.3 \cdot 10^{-3}$ *M* and the average error is 0.8%. Ba and Ca can be determined with oxalate in the ranges $1–3.3 \cdot 10^{-3}$ *M* and $1.2–5 \cdot 10^{-3}$ *M* respectively, with an error of 1%. When present together, Ba is titrated with chromate, and the sum Ba + Ca with oxalate. Mg can be titrated with NaOH in the range $8.3 \cdot 10^{-4}–5 \cdot 10^{-3}$ *M*. It interferes in the Ca determination if it is present in 10:1 ratio, and is precipitated by oxalate if present in 1:10 ratio. In a still lower ratio only Ca is determined. In all these cases Mg must be determined on a separate sample by NaOH titration. [Gio.Ser.]

1181 – Internal complexes of cadmium with glycine (in Russian). I. A. Fedorov and T. A. Balakaeva. *Zhur. Neorg. Khim.*, 5 (1960) 1533.
Cadmium may form with glycine an internal complex diglycine–Cd of the formula $Cd(Gl)_2 \cdot H_2O$, two coordination valencies being occupied by each glycine molecule, with the formation of a ring. Together with other properties, the molar conductivity is given at different concentrations, at room temperature. This complex may add one or two salt molecules, such as NH_4Cl, NaCl, KCl, $BaCl_2$, $2K_2SO_4$, NH_4Br, $CaCl_2$, CH_5N_3HCl. The molar conductivity of $Cd(Gl)_2 \cdot BaCl_2$ is given. See also following abstract. [Li.Ne.Ro.]

1182 – Cadmium–glycine compounds (in Russian). I. A. Fedorov and T. A. Balakaeva. *Zhur. Neorg. Khim.*, 5 (1960) 1522.
Molar conductance at different concentrations and at room temperature is given for the complexes of Cd and glycine of the following type: $Cd(GlH)_nX_2$. In aqueous media these complexes are not stable, as glycine may easily exchange with other groups. (See also preceding abstract.) [Li.Ne.Ro.]

1183 – High-frequency investigation of solutions containing aluminium (in German). E. Pungor and E. E. Zapp (Institute of Inorganic and Analytical Chemistry, Eötvös University, Budapest, Hungary). *Ann. Univ. Sci. Budapest. Rolando Eötvös nominatae, Sect. Chim.*, 2 (1960) 329–340.
The method described by Cruse and Nettesheim was examined by the authors, using solutions containing either aluminium halides or aluminium sulphate. Strong and weak alkalies served as titrants. The titration results were in accordance with the data given by Cruse and Nettesheim. Further, the authors present a rapid procedure for the high-frequency titration of aluminium. Essentially, free acid is measured first with barium hydroxide, then sufficient excess barium hydroxide is added to completely dissolve the aluminium hydroxide formed, and to produce excess barium hydroxide. Excess barium hydroxide is back titrated with acetic acid. The end-point appears at the aluminate value. [E.Pun.]

1184 – Conductometric study of the reaction between aluminium nitrate and alkali (in English). B. R. Guha and B. P. Gyani (Science College, Patna, India). *J. Indian Chem. Soc.*, 37 (1960) 785.
Reactions between $Al(NO_3)_3$ and alkalis ($NaOH, NH_4OH$) have been studied by means of both direct and inverse conductometric titrations. Different results have been obtained regarding the

composition of compounds formed, which are probably due to the prevailing pH, ionic concentration and ageing. By suitable choice of conditions pure $Na_2HAlO_3.Al(OH)_3$ and nearly pure $NaAlO_2$ may be formed. Freshly precipitated $Al(OH)_3$ may also be quantitatively converted into $AlCl_3$ during titration with HCl. [R.S.Sa.]

1185 – The equivalent conductance of the hexafluoro complexes of group IV (Si, Ge, Sn, Ti, Zr, Hf). R. H. Schmitt, E. L. Grove and R. D. Brown (School of Chemistry, University of Alabama, U.S.A.). *J. Am. Chem. Soc.*, 82 (1960) 5292.
The authors have measured the conductances of solutions of potassium, rubidium, and cesium salts of the hexafluoro complexes of Si, Ge, Sn, Ti, Zr, and Hf. Plots of conductance *vs.* $\sqrt{C}$ were curved as is typical for weak electrolytes. Upon correction of the conductance values for hydronium ion arising from slight hydrolysis of the complex, the above plots gave a straight line over the range of concentration studied. Limiting equivalent conductances were determined from the extrapolated plots. [R.W.Mur.]

1186 – Method of the differential conductometric titration of methylchlorosilane mixtures in non-aqueous solutions (in Russian). A. P. Kreshkov and V. A. Drosdov (D. I. Mendeleev Institute of Chemical Technology, Moscow, U.S.S.R.). *Doklady Akad. Nauk S.S.S.R.*, 131 (1960) 1345–1348.
Substances investigated are trimethylchlorosilane, dimethyldichlorosilane and methyltrichorosilane, as well as their binary and tertiary mixtures. The titrant is 0.1 *M* dimethylamino-antipyrine solution in benzene prepared from an accurately weighed amount of the reagent. The titration vessel was covered with square (1 × 1 cm) platinised platinum electrodes welded into the vessel lid. A mixture of 2 parts by volume acetonitrile and 3 parts by volume diethyl ether are introduced into the vessel, the sample dissolved in benzene is added, and the solution is titrated by 0.3 *M* ammonium rhodanide solution in acetonitrile. Thus chloride is displaced by rhodanide, ammonium chloride being precipitated. When conductivity of the mixture decreases sharply (and no more precipitate is formed), the reaction products are titrated by the dimethylamino-antipyrine volumetric solution. As the conductivity of the solution increases, inflections on the titration curve indicate various end-points for components of the sample mixture. Maximum relative errors are 2%. [Ot.So.]

1187 – A physico-chemical study of the maleate complex of trivalent cerium (in English). M. C. Saxena and A. K. Bhattacharya (University of Saugar, Sagar, India). *J. Sci. Ind. Research (India)*, 20 B (1961) 127.
Complex formation between maleic acid and cerous nitrate has been studied by means of conductance and pH measurements and also by applying Job's method of continued variation. The results obtained by the two methods suggest the formation of 1 : 1 complex between maleic acid and cerous nitrate which may be represented by the formula $Ce(C_4H_5O_5)^{2+}$. The dissociation constant *K* for the complex has been calculated to be $2.733 \cdot 10^{-3}$ at 24°. [R.S.Sa.]

1188 – High frequency titration as applied to the determination of thorium, uranium, sulfate and free acid (in English). O. Menis (Oak Ridge National Laboratory, Tenn., U.S.A.). *Nuclear Sci. Abstr.*, 15 (1961) 115, *Abstr. No.* 8663. [Red.]

1189 – Conductometric study on the precipitation of arsenites of lead as a function of the pH (in English). R. S. Saxena and Gyan Prakash Saxena (Government College, Kota, India). *Current Sci. (India)*, 30 (1961) 140.
The formation and composition of lead arsenites obtained by the interaction of lead nitrate and $NaAsO_2$ at definite pH levels, 9.85, 11.25 and 12.28 have been studied by conductometric titrations between the reactants, both by the direct and inverse methods. A distinct break in the titration curves is observed at a point corresponding to the formation of different arsenites depending upon the pH; lead metaarsenite, $Pb(AsO_2)_2$ or $PbO \cdot As_2O_3$, at pH 9.85; lead pyroarsenite having the molecular formula $Pb_2As_2O_5$ or $2PbO \cdot As_2O_3$ at pH 11.25 and normal lead orthoarsenite, $Pb_3(AsO_3)_2$ or $3PbO \cdot As_2O_3$, at pH 12.28. [R.S.Sa.]

1190 – The complex of vanadium(V) with ethylenediaminetetraacetic acid. G. Kakabadse and H. J. Wilson (Department of Chemistry, College of Science and Technology, Manchester, Gt. Britain). *Analyst*, 86 (1961) 402.
The titration of polyvanadic acid with EDTA in the presence of perchloric acid showed breaks in the conductance–volume curve near the expected end-point. The ratio of H : V ions was critical and had to exceed 5 and the pH had to be greater than 1.8. 0.002–0.007 g atoms of V per litre could be titrated with an error of not more than 5%. An alternative complexometric technique using xylenol orange as indicator was also described. [P.O.Ka.]

1191 – A study of complex formation between vanadyl sulphate and potassium salicylate (in English). A. K. Bhattacharya and S. N. Banerjee (University of Saugar, Sagar, India). *J. Sci. Ind. Research (India)*, 20 B (1961) 131.
The complex formation between vanadyl sulphate and potassium salicylate has been studied by applying the monovariation and Job's continued variation methods, the former being used in pH and conductometric studies and the latter only in conductometric investigations. The results of pH and conductance study suggest the formation of 1 : 2 complex between vanadyl sulphate and potassium salicylate and that the stoichiometry of the complex is independent of the concentrations of the reacting solutions. The dissociation constant K of the complex has the average value $6.138 \cdot 10^{-6}$ at 26°. [R.S.Sa.]

1192 – New investigations on fused $SbBr_3$ as ionising solvent (in Spanish). E. Curras Puente (Faculty of Sciences, University of Madrid, Spain). *Anales real soc. españ. fis. y quim.*, 57 B (1961) 259–276.
The behaviour of the following substances has been investigated using cryoscopy and conductometric methods: (a) sulphur, iodine, selenium; (b) 2,4,6-collidine bromide, antimony nitride and acetate, boron tribromide, oxide, sulfide, selenide and telluride of Sb(III); (c) mercuric oxide, sulfide, selenide and telluride. In case (a), simple solution is observed (red selenium being gradually transformed into the metallic form which is insoluble). According to the nature of the substances, basic, acidic or amphoteric behaviour is observed with (b) and (c). It is concluded that $SbBr_3$ can be considered as an ionising and differentiated solvent, of acidic character, and rather similar to H_2O, its dissociation reaction being $2\ SbBr_3 \rightleftharpoons SbBr_2^+ + SbBr_4^-$. The stoichiometry of the various compounds found is established. [L.Gi.]

1193 – Syncline in the conductivity diagram of the system nitric acid–sulphuric acid–sulphuric anhydride (in Russian). V. A. Usol'tseva (Department of Inorganic and Analytical Chemistry, Ivanov State Medical Institute, U.S.S.R.). *Zhur. Neorg. Khim.*, 5 (1960) 1559.
The authors have determined the specific conductivity isotherms of the system oleum–nitric acid using the following concentrations: 4.9% oleum–nitric acid in the range 0–24%; 50.9% oleum–nitric acid in the range 0–29.2%; 62% oleum–nitric acid in the range 0–34.3%. The corrected conductivity has been calculated by introducing the viscosity for the system 34.8% oleum–nitric acid in the range 0–100%.
The presence of the nitronium hydrodisulphate complex has been demonstrated by this method, showing that it behaves as an electrolyte in sulphuric acid solutions. The determinations were made by a compensation method at 20°. [Li.Ne.Ro.]

1194 – Sulphuric acid solvent system. II. Conductivity measurements on solutions of some acids. J. Barr, R. J. Gillespie and E. A. Robinson (Department of Chemistry, McMaster University, Hamilton, Canada). *Can. J. Chem.*, 39 (1961) 1266.
The conductivity of $HClO_4$, HSO_3F, HSO_3Cl, HPO_2F_2, $HAs(HSO_4)_4$, CH_3SO_3H and CF_3CO_2H were measured in sulphuric acid. HSO_3F, HSO_3Cl, $HAs(HSO_4)_4$ and probably $HClO_4$ behave as acids, CF_3CO_2H as a non-electrolyte and HPO_2F_2 and probably CH_3SO_3H as bases. These acids in the sulphuric acid system decrease in strength in the order $HSO_3F > HAs(HSO_4)_4 > HSO_3Cl > HClO_4$ — the acid dissociation constants were determined. [D.S.Ru.]

1195 – Aquo–oxalate–sulphate complexes of uranium (in Russian). I. I. Chernyaev, V. A. Golovnya and R. N. Shchelokov ('N. S. Kurnakov' Institute of General and Inorganic Chemistry, Academy of Sciences, U.S.S.R.). *Zhur. Neorg. Khim.*, 5 (1960) 1454.
The molar conductivity at different concentrations and at room temperature is given for the following new complexes: $K_2[UO_2(C_2O_4)(SO_4)(H_2O)_2]H_2O$; $Rb_2[UO_2(C_2O_4)(SO_4)(H_2O)_2]$; $Cs[UO_2(C_2O_4)(SO_4)(H_2O)_2]$; $Cs(NH_4)[UO_2(C_2O_4)(SO_4)(H_2O)_2]$.
The stability of these complexes is compared with that of aquo–oxalate and of aquo–sulphate complexes of uranium. By comparison of the conductivity values in aqueous solution of these complexes, their stability is observed to decrease in the order: $[UO_2(C_2O_4)_2(H_2O)_2]^{2-} > [UO_2(C_2O_4)(SO_4)(H_2O)_2]^{2-} > [UO_2(SO_4)_2(H_2O)_2]^{2-}$. [Li.Ne.Ro.]

1196 – Determination of free acid in uranium sulfate solutions by conductometric titration. G. Goldstein (Oak Ridge National Laboratory, Tenn., U.S.A.). *Nuclear Sci. Abstr.*, 15 (1961) 115, *Abstr. No.* 8666. [Red.]

1197 – Complexes of Mn(III) with halo-derivatives of salicylic acid (in Russian). S. Z. Makarov and F. D. Glikina (Municipal Pedagogic Institute 'Potemkin', Moscow, U.S.S.R.). *Zhur. Neorg. Khim.*, 5 (1960) 2229.
Together with other chemico-physical properties, the authors have determined the molar conduc-

tivity in ethyl alcohol of six complexes of Mn(III) with 5-Cl-salicylic acid, 5-Br-salicylic acid and 5-I-salicylic acid. These complexes were separated for the first time in a crystalline state.
[Li.Ne.Ro.]

1198 – High-frequency titrations. I. Acid-base and precipitation titration with particular respect to the lower limit of determination of concentration (in German). E. Pungor and L. Balázs (Institute of Inorganic and Analytical Chemistry, Eötvös University, Budapest, Hungary). *Ann. Univ. Sci. Budapest. Rolando Eötvös nominatae, Sect. Chim.*, 2 (1960) 305–313.
Using a high-frequency titrimeter operated at 130 Mc/s, it was possible to determine hydrochloric acid down to a limit value of 1 μg/ml, acetic acid to 20 μg/ml, chloride to 2 μg/ml and sulphate to 10 μg/ml, respectively. The titration curves obtainable with ammonium hydroxide in the case of polybasic organic acids are given. The curves changed as a function of the dielectric constant of the solution. To determine sulphate, a solution of barium acetate was used. A precipitate of barium sulphate in ethanol was used in order to promote the formation of barium sulphate crystals, and to suppress the solubility of the precipitate. [E.Pun.]

1199 – High-frequency titrations. II. Determination of sodium carbonate and bicarbonate in the presence of each other with an end-point indication by high-frequency methods (in German). E. Pungor and L. Balázs (Institute of Inorganic and Analytical Chemistry, Eötvös University, Budapest, Hungary). *Ann. Univ. Sci. Budapest. Rolando Eötvös nominatae, Sect. Chim.*, 2 (1960) 315–317.
Carbonate was titrated to bicarbonate with acetic acid. In a separate sample the combined sum of carbonate and bicarbonate was determined by adding excess hydrochloric acid to the solution, boiling the mixture, and then measuring the excess of hydrochloric acid with 0.1 *N* sodium hydroxide. In this titration a high-frequency measuring instrument served as an indicator. (See preceding abstract). [E.Pun.]

1200 – High-frequency titrations. III. Iodometric titrations with high-frequency indication (in German). L. Balázs and E. Pungor (Institute of Inorganic and Analytical Chemistry, Eötvös University, Budapest, Hungary). *Ann. Univ. Sci. Budapest. Rolando Eötvös nominatae, Sect. Chim.*, 2 (1960) 319–324.
A method was evolved by the authors for the determination of sulphite, arsenite and antimonite with high-frequency indication. In essence this method consists of an oxidation by iodine solution, while an iodine solution in methanol serves as titrant. In this way it is possible to attain a stable conductance in the solution, after reaching the end-point. The titration curves have a horizontal section after the end-point. (See preceding abstracts). [E.Pun.]

1201 – Para- and diamagnetic rhenium(IV) complexes. III. Complex compounds of rhenium (IV) with organic hydroxy-acids (in English). B. Jeżewska-Trzebiatowska and S. Wajda (Department of Inorganic Chemistry, University, Wroclaw, and Institute of Physical Chemistry, Wroclaw, Poland). *Bull. acad. polon. sci., sér. sci. chim.*, 9 (1961) 57–64.
The complex compounds of rhenium(IV) with citric and tartaric acids have been prepared *i.e.* compounds $K_2[Re_2O(OH)_6(Citr)_2]$ and $K_4[Re_2O(OH)_6(Tart)_2]$, the composition of which was established by chemical analysis. The binuclear structure of these compounds was confirmed on the basis of equivalence conductance measurements, and their interpretation on the basis of the Walden–Ostwald rule and Sheldlovsky equation, and calculation of coefficient *a* from the Debye–Onsager equation. Complexes investigated were found to be diamagnetic due to spin–spin coupling through the oxygen bridge, which was called "inner molecular anti-paramagnetism". The absorption spectra of complexes were investigated in the range 380–720 mμ. They show no definite bands and are quite similar to each other. [Ad.Hu.]

1202 – Para- and diamagnetic rhenium(IV) complexes. IV. Rhenium(IV) complexes with phenol carboxylic acids (in English). B. Jeżewska-Trzebiatowska, S. Wajda and W. Wojciechowski (Department of Inorganic Chemistry, University, Wroclaw and Institute of Physical Chemistry, Wroclaw, Poland). *Bull. acad. polon. sci., sér. sci. chim.*, 9 (1961) 65–69.
The rhenium(IV) complexes with gallic and salicylic acids were prepared. Their formulae $Me_4[Re_2O(OH)_6(Gal)_2]$ and $Me_2[Re(OH)_4(Sal)_2]$ were established on the basis of their magnetic properties, measurements of equivalent conductance and chemical analysis. The former compound in solution as well as in the solid phase is diamagnetic, the latter is paramagnetic (μ = 3.56 BM). If the ligand is a weak base (anions of moderately strong acids) the hydroxy groups have amphoteric character, and oxygen bridges and subsequently binuclear complexes can be formed. If ligands are strongly basic, the OH groups cannot undergo amphoteric dissociation and no binuclear complexes are formed. (See preceding abstract). [Ad.Hu.]

1203 – Investigation of the formation of metal complexes by a high-frequency method (in German). E. E. Zapp and E. Pungor (Institute of Inorganic and Analytical Chemistry, Eötvös University, Budapest, Hungary). *Ann. Univ. Sci. Budapest. Rolando Eötvös nominatae, Sect. Chim.*, 2 (1960) 341–349.
In the investigations by Hara, the authors found controversial data regarding the composition of the complex described by him. According to the authors' results, it is not possible to draw any conclusions in respect to the composition of the complexes examined by Hara from titration curves obtained by high-frequency titrations. At the same time the authors found that the high-frequency titration of iron and thorium can readily be carried out with EDTA, as in the case of these elements, high-frequency titration indicates the acid liberated during titration proper. [E.Pun.]

1204 – Metallic complexes of dimethyl-*o*-(methylthio)phenylarsine. IV. Complexes of platinum. B. Chiswell and S. E. Livingstone (Department of Inorganic Chemistry, University of New South Wales, Sydney, Australia). *J. Chem. Soc.*, (1960) 1071–1074.
The nature of the complexes formed has been determined on the basis of spectrophotometric and conductometric data. It has been found that the platinum atom can be either quadri-covalent or quinque-covalent (the latter case being observed in nitrobenzene in the presence of halide ions, acting as fifth ligand). [L.Gi.]

1205 – Preparation and properties of deeply coloured, electrically conducting polymers. P. V. French, L. Roubinek, and A. Wasserman (University College, London W. C. 1, Great Britain). *J. Chem. Soc.*, (1961) 1953–1963.
Various properties of unsaturated polymers obtained from cyclopentadiene and four of its derivatives were studied. These polymers can undergo reversible reaction with protons; the formation of ion-pairs by proton-transfer is demonstrated by measurements of electrical conductance. Values for the dissociation constants have been calculated for benzene at 25°. [L.Gi.]

1206 – Studies in acetyl bromide as a polar solvent. I. Solubility of substances, formation of solvates and electrical conductance of solutions (in English). R. C. Paul, S. S. Sandhu and J. S. Bassi (Panjab University, Chandigarh, India). *J. Indian Chem. Soc.*, 38 (1961) 81.
The solubilities of several substances including a few Lewis acids, bromides, and organic tertiary bases have been determined in acetyl bromide and the formation of solvates has been investigated by taking into consideration the electrical properties of the solutions. The specific conductance of the Lewis acids, bases and quarternary ammonium bromides has been determined in acetyl bromide at 30°. The specific conductance of these solutions indicates their strong ionisation in acetyl bromide. The solvates of pyridine, isoquinoline, β-picoline and γ-picoline also enhance the conductance of acetyl bromide. See also following abstract. [R.S.Sa.]

1207 – Studies in acetyl bromide as a polar solvent. IV. Conductometric titrations in acetyl bromide (in English). R. C. Paul, Jit Kaur and S. S. Sandhu (Panjab University, Chandigarh, India). *J. Indian Chem. Soc.*, 38 (1961) 93.
The existence of solvo-acids, solvo-bases and ansolvo-bases in acetyl bromide has been confirmed by means of conductometric titrations. Stannic bromide and antimony tribromide have been used as solvo-acids. Solutions of α-picoline, quinoline, isoquinoline and dimethyl aniline have been used as solvo-bases and the quaternary ammonium halides, *viz.*, tetraethylammonium bromide, triethylbenzylammonium bromide, dimethylethylphenylammonium bromide, and dimethylphenylbenzylammonium bromide, have been used as ansolvo-bases. The breaks in the conductometric titration curves corresponding to different acid–base molar ratios have been noted, indicating the formation of acid or normal salts. The formation of a number of complexes has been indicated and is explained on the basis of existence of ionic species in solutions of acetyl bromide. (See also preceding abstract). [R.S.Sa.]

1208 – Electrolyte–solvent interaction. IX. Tetra-alkylammonium tetraphenylborides in acetonitrile–carbon tetrachloride mixtures at 25°. Donald S. Berns and Raymond M. Fuoss (Sterling Chemistry Laboratory, Yale University, New Haven, Conn., U.S.A.). *J. Am. Chem. Soc.*, 82 (1960) 5585.
The conductances of several tetra-alkylammonium tetraphenylborides (methyl, ethyl, *i*-propyl, and *n*-butyl) have been measured in acetonitrile–carbon tetrachloride solutions (D range, 10–36) at 25°. Values of limiting conductances and association constants (calculated by computer techniques) fall in the expected order; extrapolated hydrodynamic radii for the four cations are 2.37, 2.75, 3.31, 3.84, respectively. These values are in agreement with values derived by electrostatic theory from association constants. [R.W.Mur.]

1209 – Activity coefficient and conductivity measurements of high-charge (3–1, 1–3, 3–2)

electrolytes. I. R. A. Wynveen, J. L. Dye and C. H. Brubaker, Jr. (Kedzie Chemical Laboratory, Michigan State University, East Lansing, Mich., U.S.A.). *J. Am. Chem. Soc.*, 82 (1960) 4441.
By means of isopiestic comparison with potassium chloride solutions, the authors have measured the mean activity and osmotic coefficients for aqueous solutions of $Co(en)_3(NO_3)_3$, $Co(pn)_3(ClO_4)_3$, $K_3Co(CN)_6$, and $Co(en)_3(SO_4)_3$. Low values of *a* were required to fit the data to the Debye–Hückel equation. Conductivity measurements were made for the same solutions and again low *a* values (agreeing with those from the isopiestic measurements) were necessary to fit the experimental data to theory. It is noted that inadequacies in the theory for both experiments are apparently adsorbed in the *a* parameter. (See also following abstract). [R.W.Mur.]

1210 – Activity coefficients and conductances of high-charge (4–1, 1–4, 1–2)electrolytes. II. K. O. Groves, J. L. Dye and C. H. Brubaker, Jr. (Kedzie Chemical Laboratory, Michigan State University, East Lansing, Mich., U.S.A.). *J. Am. Chem. Soc.*, 82 (1960) 4445.
The mean activity and osmotic coefficients of aqueous solutions of $Pt(pn)_3Cl_4$, $[NMe_4]_4Mo(CN)_8$, $K_4W(CN)_8$ and $K_2Pt(CN)_4$ have been measured by means of isopiestic comparisons with potassium chloride solutions. The methods of Scatchard and Prentiss and graphical integration of the Gibbs–Duhem equation were used to evaluate the data; the activity coefficients were the same for the two methods of calculation but values of the parameter *a* differed. The conductances of solutions of the above electrolytes were also measured and deviations from the Onsager limiting law were observed. [R.W.Mur.]

1211 – Single ion conductances in non-aqueous solvents. Raymond M. Fuoss and Ernest Hirsch (Sterling Chemistry Laboratory, Yale University, New Haven, Conn., U.S.A.). *J. Am. Chem. Soc.*, 82 (1960) 1013.
The authors have carried out conductance measurements on tetrabutylammonium tetraphenylboride (I) in the solvents propylene carbonate (dielectric constant 65.1) and mixtures of nitrobenzene and carbon tetrachloride (dielectric constant range 34.7–7.8). The nearly equal volumes of the cation and anion of (I) permits evaluation of single ion conductances by taking one-half the limiting equivalent conductances. Single ion and limiting conductances of (I) are given for a range of concentrations in each solvent. The distance parameter, *a*, was evaluated by three independent methods of calculation (from limiting conductance, limiting curvature of phoreograms, and association constants). The values of *a* obtained were in agreement with one another, giving an average of 7.1 Å. [R.W.Mur.]

1212 – Determination of alkaloids in decoctions of Ipecacuanha root by the conductometric method (in Polish). W. Wiśniewski and S. Jablonski (Department of Applied Pharmacy, Academy of Medicine, Warsaw, Poland). *Acta Polon. Pharm.*, 18 (1961) 119–124.
A conductometric method for the determination of the alkaloid content in decoctions of Ipecacuanha root has been developed. To the concentrated decoction 1 ml of 10% ammonia was added, and the solution was extracted with $CHCl_3$. After evaporation of $CHCl_3$ the residue was dissolved in 20 ml ethanol and 5 ml water was added. The prepared solution was titrated conductometrically with 0.01 or 0.005 *N* HCl. For one determination 2.5 g of decoction is sufficient if the alkaloid content is not less than 1%. [Ad.Hu.]

See also abstracts nos. 961, 968, 975, 989, 992, 1122, 1132, 1143, 1150.

6. Electrolysis

1213 – Réduction électrolytique d'oxydes et d'hydroxyde de cuivre en suspension aqueuse. J. Saelemaekers et A. Van Tiggelen (Laboratoire de chimie inorganique, Université de Louvain, 96 rue de Namur, Louvain, Belgique.). *Bull. soc. chim. France*, (1961) 1295–1302.
Les auteurs étudient la réduction électrochimique de films et de précipités d'oxydes et d'hydroxyde de cuivre.
Films d'oxyde cuivreux.–Ils sont préparés par oxydation anodique à 15°, d'une électrode de cuivre en milieu alcalin (soude normale). Leur réduction, en milieu neutre, ne donne qu'une vague, sur la courbe intensité tension électrique. Cette vague peut être identifiée à celle de $Cu(OH)_2$. En milieu sodique l'interprétation des phénomènes—plus complexes—nécessite qu'on fasse appel à l'existence de l'ion complexe $Cu(OH)_4^{2-}$.
Films de CuO–Ils sont préparés par oxydation anodique d'une électrode de cuivre à 45°. Les

courbes intensité tension électrique ne semblent pas pouvoir s'interpréter sans l'existence du composé $Cu(OH)_4^{2-}$.
Précipité de CuO – Il est soit disposé sur une cathode horizontale, soit maintenu en suspension par agitation de la solution (la cathode plonge alors dans la solution et reste fixe). La nature de l'électrode n'intervient pas et l'évolution de la tension électrique de réduction en fonction du pH suit les lois théoriques (entre pH 11 et pH 14).
Précipité de Cu_2O. – Celui-ci n'est réduit pas (à une électrode de platine et dans certaines conditions de mesure qu'à partir de pH 13.3). Le complexe $Cu(OH)_4^{2-}$ interviendrait dans la réaction.
Précipité de $Cu(OH)_2$ – La tension de décharge est alors fortement affecté par la nature de l'électrode (Pt, Cu, Hg). Il semble, d'autre part, que les réductions précédentes se fassent en partie par l'intermédiaire des atomes d'hydrogène adsorbés sur l'électrode. [J.Des.]

1214 – Evaluation of the electrodeposition method for the determination of enriched uranium in urine. R. L. Hancock and G. S. Golden (Combustion Engineering Inc., Nuclear Div., Windsor, Conn., U.S.A.). *Nuclear Sci. Abstr.*, 15 (1961) 770, *Abstr. No.* 5955. [Red.]

1215 – The electrolytic determination of carbon monoxide. P. J. Ovenden (National Coal Board, Scottish Divisional Laboratory, Glasgow Road, Edinburgh, Scotland). *J. Electroanal. Chem.*, 2 (1961) 80.
The electrometric determination of gaseous carbon monoxide is discussed. A method is described for the continuous estimation of carbon monoxide in air, using a vibrating Pd micro-electrode which is intermittently polarised anodically whilst the air sample is passing through the cell. A limiting diffusion current is observed which bears an approximately linear relationship to the partial pressure of carbon monoxide in mixtures of carbon monoxide and oxygen. [Author]

1216 – Dual cathode technique for the electrolytic reduction of *m*-dinitrobenzene to 2,4-diaminophenol (in English). K. S. Udupa, G. S. Subramian and H. V. K. Udupa (Central Electrochemical Research Institute, Karaikudi 3, India). *Bull. Acad. Sci., Sér. sci. chim.*, 9 (1961) 419–424.
A new efficient technique has been developed for electrolytic reduction of *m*-dinitrobenzene to 2,4-diaminophenol. On the basis of cathodic polarisation investigations it was found that the best efficiency can be obtained if in the first stage, corresponding to the amount of current equal to 4 F, an amalgamated monel cathode is used, which is later replaced by the copper electrode in the final stage. Stationary disc electrodes can be used as well as a rotating one, provided the current density is not too high. 50% sulphuric acid was used as the electrolyte. The maximum yield of 2,4-diaminophenol sulphate was about 65%. [Ad.Hu.]

See also abstract no. 1263.

7. Coulometry

1217 – Electroanalysis by isotopic dilution. I. Microcoulometer for radioactive silver and the determination of silver (in German). J. Růžička (Institute of Nuclear Chemistry, Charles University, Prague, Czechoslovakia). *Collection Czechoslov. Chem. Communs.*, 25 (1960) 199–205.
A coulometer is proposed in which radioactive metal is precipitated with 100% current efficiency on an electrode, whose activity is then measured. When using a scintillation technique and ^{110}Ag, a range of measurement of 0.05–0.80 coulombs can be reached for the range of current densities 0.03–0.30 mA/cm², the mean error being ± 1.8%. A method for the determination of silver is proposed for milligram and submilligram amounts, in which activities of deposits are compared after precipitation by electrolysis in two electrolytic vessels connected in series, and containing solutions of similar chemical, but different isotope composition. The metal amounts deposited are then equivalent as long as current efficiency is kept less than 100%. The mean relative error is 2%. [Ot.So.]

1218 – Coulometric determination of Sn with electrolytically generated I_2: application to analysis of zircaloy. R. D. Caton Jr. and H. Freund (Oregon State College, U.S.A.). *Symposium on Newer Metals, A.S.T.M. Special Techn. Publ. No.* 272, American Society for Testing Materials, Philadelphia, 1960, p. 207. [Red.]

1219 – Indirect coulometric titration of reducible organic compounds by ceric ion (in English). T. Takahashi and H. Sakurai. *Nuclear Sci. Abstr.*, 15 (1961) 117, *Abstr. No.* 8682. [Red.]

1220 – The residual quantity of electricity in coulometry at controlled electric tension: bromide oxidation on a polished Pt electrode (in French). J. Badoz-Lambling (Laboratoire de Chimie Analytique, Ecole Supérieure de Physique et de Chimie Industrielles, Paris, France). *J. Electroanal. Chem.*, 1 (1959/1960) 44.
By means of current–electric tension curves it is possible to select the electric tension most suitable for electrolysis in a given coulometric determination. Selection of a suitable electric tension is the best way of eliminating the effect of extraneous electrochemical reactions during the electrolysis. This elimination is never complete, however, and the residual quantity of electricity resulting from these reactions renders the determinations less accurate. This residual quantity can easily be calculated if no chemical reactions take place between the substances present during the electrolysis. If reactions do occur then a calibration procedure is carried out, using known solutions.
[Authors]

1221 – Coulometric determination of periodate (in German). H. L. Kies and J. J. Buyk (Analytical Chemistry Laboratory, Technical College, Delft, The Netherlands). *J. Electroanal. Chem.*, 1 (1959/1960) 176.
The coulometric titration of periodate performed in a solution that is 0.1 *M* with respect to iron (III) sulphate and 0.5 *M* with respect to sulphuric acid, gives good results for quantities between 0.06 and 15 mg.
Iodate does not interfere with the determination, except when it is present in a large excess.
[Authors]

1222 – Coulometric titration of uranium in HNO_3 solution. M. O. Fulda (Du Pont de Nemours, Savannah River Laboratory, Aiken, S.C., U.S.A.). *Nuclear Sci. Abstr.*, 15 (1961) 18, *Abstr. No.* 123. [Red.]

1223 – A polarographic and coulombometric study of sulphuric and hydrochloric solutions of U(VI) (in Russian). E. A. Kanevskij and G. R. Pavlovskaya. *Zhur. Neorg. Khim.*, 5 (1960) 1964.
A coulombometric method is employed in the study of the process of reduction of U(VI) on the dropping mercury electrode in sulphuric solution. This method allows the determination of the number of electrons which participate in the processes which are responsible for the formation of the first, second and third reduction waves. *Z* is derived by the method of Stromberg and Markacheva, and is found to be equal to 1 for a 0.0007 *M* solution of UO_2SO_4 in 0.005 *N* H_2SO_4 and 1 *N* K_2SO_4; it is equal to 1.5 in 4 *N* H_2SO_4. The disproportionation rate of U(V) in sulphuric solution is shown to depend essentially upon the concentration of HSO_4^- ions. A considerable shift is observed in the half-wave value of the first reduction wave of U(VI) in K_2SO_4 solution, as the concentration of the latter is varied from 0.01 to 1.00 *N*. By this method the difference between the number of added groups in the oxidized and reduced forms is found to be 1.4. In the given solution the fundamental reduction process can thus be expressed by the equation

$$UO_2SO_4 + e^- \rightleftarrows U_2^+ + SO_4^{2-}$$

[Li.Ne.Ro.]

See also abstracts nos. 980, 990, 1010.

8. Electrophoresis

1224 – Electromagnetophoresis (in Polish). J. Kowalczyk and T. Pompowski (Department of Technical Analysis, Politechnika, Gdańsk, Poland). *Wiadomości chem.*, 15 (1961) 107–129.
A review article surveying the theory and possibilities of using electromagneto-kinetic phenomena, with 23 references. [Ad.Hu.]

1225 – Changes of pH in the course of paper electrophoresis and their influence on ion separation (in Polish). Z. Szpenar (Department of Technical Analysis, Politechnika, Gdańsk, Poland). *Chemia anal.*, 6 (1961) 187.
Changes of pH were investigated in paper electrophoresis when the paper strips were directly

dipped into solutions in which electrodes were placed. Large changes were observed in solutions of salts of strong acids and strong bases. Also, changes were observed in some buffer solutions, especially in borate buffers. This should be taken into account when pH sensitive protein separations are carried out. Also, pH changes have an important influence on the separation and detection of gold by means of the benzidine reaction. [Ad.Hu.]

1226 – Methode d'électrophorèse en gradient de densité comme nouvelle technique en virologie (en anglais). R. Cramer et H. Svensson (Laboratoire Pasteur, Institut du Radium, Paris, France, et Départment de Bactériologie, Institut Karolinska, Stockholm, Suède). *Experientia*, 17 (1961) 49.
Les méthodes chimiques et physico-chimiques sont quasi impuissantes lorsqu'il s'agit de séparer et de doser les virus car la masse de ceux-ci est extrêmement faible et parce qu'ils évoluent dans des milieux particulièrement complexes. La méthode électrophorétique en gradient de densité par contre permet d'obtenir d'intéressants résultats. Preuve en sont les diagrammes éléctrophorétiques donnés par les auteurs. Une description de l'appareillage et quelques schémas complètent cet exposé. La méthode électrophorétique en gradient de degré permet aussi la purification des virus (virus de la poliomyélite). Cette méthode pourra aussi s'appliquer à la solution d'autres problèmes biologiques. [De.Mo.]

1227 – Séparation d'isotopes par électromigration en contre-courant dans des systèmes d'halogénures fondus. J. Périé, M. Chemla et M. Gignoux (Laboratoire de physique nucléaire du Collége de France, Paris, France). *Bull. soc. chim. France*, (1961) 1249–1256.
Les auteurs présentent une méthode de séparation des deux isotopes du lithium. Ils opèrent par électromigration dans un mélange fondu de bromures de lithium et de potassium. On constate, en effet, que – bien que les mobilités des ions lithium et potassium purs soient légèrement différentes – le rapport BrLi/BrK, dans le compartiment anodique, se stabilise rapidement (10 jours) tandis que le rapport $^{7}Li/^{6}Li$ continue ensuite, à croitre exponentiellement avec le temps.
Les auteurs décrivent en détail les dispositifs expérimentaux utilisés (cellule en pyrex – forme en U, diaphragme en poudre de zircon – grains de 0.1 mm de diamètre, circuit de récupération du brome, dispositifs de sécurité, etc.).
Ainsi en électrolysant sous 70 V, 0.7 A pendant 6 semaines un mélange fondu à 450° dans lequel BrLi/BrK = 2.12 et $^{7}Li/^{6}Li$ = 11.7, on obtient dans le compartiment anodique un mélange dans lequel BrLi/BrK = 1.75 et $^{7}Li/^{6}Li$ = 3500. Pour cette expérience on indique les courbes de répartition des rapports $^{7}Li/^{6}Li$, $^{39}K/^{41}K$ et BrLi/BrK le long du diaphragme. Des conclusions analogues peuvent être obtenues pour des mélanges BrLi/BrNa. A partir des resultats précédents, les auteurs déduisent des hypothèses sur la structure des sels fondus [les ions M^{+} ne pourraient se déplacer que s'ils ne sont pas engagés dans des combinaisons $MBr_n^{(n-1)-}$. Ces hypothèses permettent d'interpréter certaines expériences précédemment décrites dans la $MBr_n^{(n-1)-}$ littérature. [J.Des.]

1228 – Paper electrophoresis of uni- and poly-valent alcohols (in German). H. Berbalk (Institute for Organic Chemistry, Technical College, Vienna, Austria). *Monatsh. Chem.*, 90 (1959) 24–28.
A separation of uni- and poly-valent primary and secondary aliphatic and araliphatic alcohols is described. The alcohols are treated with NaOH, CS_2 and water and the aqueous solution of xanthogenates obtained is subjected to paper electrophoresis. Best results are obtained when the solution is buffered (Veronal buffer pH = 9). Migration rates are referred to methanol (methyl xanthogenate). They show a decrease with increasing number of C atoms, and an increase when the chain is branched. Introduction of a second OH group also increases the migration rate. [C.I.Moo.]

1229 – Acrylamide-gels as supporting media for electrophoresis. S. Raymond and L. Weintraub (Pepper Laboratories, University of Pennsylvania, Philadelphia, Pa., U.S.A.). *Science*, 130 (1959) 711.
More definite, clear-cut bands are given if the gel obtained by the polymerization of acrylamide or N,N'-methylene-bis-acrylamide, conveniently buffered, is used as the supporting medium; its transparency is high, it is also colourless so that direct absorption measurements can be made. The various bands can be stained in the usual way by bromophenol blue. After drying, the film obtained can be conveniently stored.
The method has the advantages of higher resolution and speed. Some separations using albumin serum, or globulin or haemoglobin have been conveniently performed. [Ca.Cas.]

1230 – An improvement to the lead tetra-acetate detection of sugar alcohols in paper electrophoresis. K. Sampson, F. Schild and R. S. Wicker (Research Department, Howards of Ilford Ltd., Ilford, Essex, Gt. Britain). *Chem. & Ind.*, 3 (1961) 82.
The method using lead tetra-acetate to develop the sugar and sugar alcohol spots suffers from two

disadvantages. The lighter spots on a brown background exhibit poor contrast of trace quantities and the spots which are developed are not permanent.
The authors recommended the addition of rosaniline in the development to produce a red spot on a grey–white background. The spots were found to be permanent and twice as sensitive when used on sorbitol. [D.S.Ru.]

1231 – Electrophoresis of soluble proteins in agar gel (in Russian). A. T. Ilkov and T. Nikolov. *Voprosy̆ Med. Khim.*, 5 (1959) 388–392.
Blood serum proteins were separated by electrophoresis on agar gel in a barbitone buffer (μ = 0.05; pH 8.6) with a potential gradient of 2.5 V/cm. After electrophoresis the plate was immersed twice in a bath of 0.2 *N* acetic acid and kept for 8–12 h at 37°. The plates were dried and coloured with Amido black 10 B (5 h) and decolorised by immersion in 2% acetic acid containing 2% glycerol. By photometric study of the dried plates β_1^- and β_2^- globulins were found in human and animal sera together with the normal albumin and globulins obtained by paper electrophoresis. An α_3 fraction was also found between α_2 and β_1 in some human sera. Even more protein fractions were observed in sera from dogs. β_2 and γ globulins were also fractionated in some cases. The soluble proteins and enzymes extracted from different tissues have also been examined by this technique. [Gio.Ser.]

1232 – ^{131}I as "amplifier" in paper electrophoresis of proteins. O. P. Foss (Ulleval Hospital, Central Laboratory, Oslo, Norway). *Scand. J. Clin. Lab. Invest.*, 11 (1959) 169.
The paper sheet is previously dipped in the buffer (0.1 *M* Barbital, pH = 6.8, containing 10% human serum) in order to saturate it with respect to proteins, then the proteins to be studied, after treatment with ^{131}I, are submitted to electrophoresis: detection of the bands is achieved by means of radioautography. Owing to the sensitivity of this method, very small amounts of proteins can be detected. [Ca.Cas.]

1233 – Molecular interactions in β-lactoglobulin. II. Ultracentrifugal and electrophoretic studies of the association of β-lactoglobulin below its isoelectric point. Robert Townend, R. J. Winterbottom, and Serge N. Timasheff (Eastern Regional Research Laboratory, Philadelphia, Pa., U.S.A.). *J. Am. Chem. Soc.*, 82 (1960) 3161.
A study of the ultracentrifugal and electrophoretic behaviour of several samples of β-lactoglobulin in the pH range 3.5–5.2 has been performed to determine the degree of aggregation in this range. Analysis of data by the Gilbert theory indicates the presence of trimers, tetramers, and pentamers. [R.W.Mur.]

1234 – Improved method for the determination of haemoglobin A_2 by starch-gel electrophoresis (in English). C. A. J. Goldberg and A. C. Ross (William Pepper Laboratory of Clinical Medicine, University of Pennsylvania, Pa., U.S.A.). *Clin. Chem.*, 6 (1960) 254–262.
A method previously described by the same author (*Clin. Chem.*, 4 (1958) 484) has been modified. The accuracy of the method has been improved. [Gio.Ser.]

1235 – Electrophoretic behaviour of haemoglobins in agar gel. W. B. Gratzer and G. H. Beaven (Medical Research Council Laboratory, Hampstead, London, Gt. Britain). *J. Chromatog.*, 5 (1961) 315.
The following conclusions have been deduced from comparative experiments: (1) the best type of agar is Defco Bacto Agar; (2) the thickness must be restricted to *ca.* 1 mm, and voltage across the cell must be maintained below 2 V/cm (avoidance of heating effects); (3) the optimal duration for the best distribution of zones is about 4 h; (4) it is desirable to use concentrated haemolysates, in order to reduce retardation by dilution; (5) equilibration of the samples and the mode of their application is not very important; (6) the buffer must be relatively dilute. Citrate and EDTA buffers, and unbuffered NaCl give good results.
The mechanism of separation has been investigated, comparing sequences observed with various methods, and analyzing the effect of pH. An adsorption mechanism is proposed, which allows the interpretation of other experimental features, such as the retardation of the zone with time. [L.Gi.]

1236 – Electrophoresis studies on blood plasma esterases. III. Conclusions (in English). Klas Bertil Augustinsson (Institute of Organic Chemistry and Biochemistry, University of Stockholm, Sweden). *Acta Chem. Scand.*, 13 (1959) 1097.
A discussion is given of the results obtained in a comparative study of the esterases present in the plasmata from 27 various vertebrates. Each species has its own esterase pattern, and within each of the three groups of esterases, arylesterases (A-esterases), aliesterases (B-esterases) and cholinesterases (C-esterases), there are variations in the properties of the individual enzymes. Arylester-

ase is the predominant esterase in mammalian plasmata, and is absent in the plasmata of birds, reptiles, amphibians and fish. Aliesterase (lipase) is the main esterase of the plasmata of lower vertebrates, and is not present in human, monkey, dog, ruminant, cock, or turtle plasmata. A propionyl-aliesterase is considered to be the most primitive type of esterase present in vertebrate plasmata, and other esterases including the various types of aryl- and cholinesterases are suggested to be phylogenetically evolved from such an esterase. The esterase present in turtle plasma is of an intermediate stage. The physiological function and origin of the plasma esterases are briefly discussed. The plasma protein patterns of the little piked whale, sea scorpion and mackerel are illustrated.
The experimental conditions were as follows: 5 ml plasma was fractionated on cellulose columns for 30 h in Veronal buffer (pH = 8.4, I = 0.1) at a voltage of 260 V and a current of 60 mA. The mobility of the human plasma protein is given in $cm^2\ V^{-1}sec^{-1} \cdot 10^{-5}$. [Sv.Li.]

1237 – Paper electrophoresis and chemical analysis of extracts of steer hide corium and of whole steer hide. C. Deasy (University of Cincinnati, Ohio, U.S.A.). *J. Am. Leather Chemists Assoc.*, 55 (1960) 258–271.
Steerhide–corium extracts are prepared as previously described (*ibid.*, 54 (1959) 503). For preparing whole steer hide extracts, hide from a freshly slaughtered steer is frozen for one week. The hide is then cut into pieces and extracted successively with 5% NaCl soln, 0.1 *M* citrate buffer, 0.1 *M* Na_2HPO_4, $Ca(OH)_2$ soln, and 10% $CaCl_2$ soln. After concentration, the extracts are analysed for glycoproteins by a modification of the procedure of Grönwall and Köiw (*Scand. J. Clin. & Lab. Invest.* 4 (1952) 244). Little or no glycoproteins are contained in corium extract, whilst whole hide is shown to contain large amounts. [Gio.Ser.]

1238 – Quantitative determination of 5-hydroxytryptophan, 5-hydroxytryptamine and 5-hydroxyindol-3-ylacetic acid by paper electrophoresis (in German). A. Carcasona and others (Institute for Neuropathology, Bonn University, Germany). *Klin. Wochschr.*, 38 (1960) 457–460.
In three different buffers at different pH's (barbitone pH 8.6, acetate pH 5.05 and phosphate pH 7), 5-hydroxytryptamine travels towards the cathode, 5-hydroxyindol-3-ylacetic acid towards the anode and 5-hydroxytryptophan remains stationary. A procedure is described for the paper electrophoretic separation of the three substances. The spots are detected by spraying the paper with *p*-dimethylaminobenzaldehyde soln. in *n*-butanol (1 : 4) and heating at 60° for 20 min. The colour is measured on the paper at 540 mμ. [Gio.Ser.]

1239 – Effect of minute amounts of DDT in food on blood plasma and liver changes in rats (in Polish). T. Dabrewski, S. Zawistewski and J. Wierschowski (Department of Hygiene of Nutrition and Food, School of W.S.S.E. and Dept. of Histology and Embryology, Academy of Medicine, Gdańsk, Poland). *Roczniki Państwowego Zakladu Hig.*, 12 (1961) 55.
The influence of DDT (15–45 mg/day/rat) in the food of rats was investigated. The blood serum was analysed by means of paper electrophoresis, and the increase of biological activity in the β and γ fraction was observed. The results were compared with histological, enzymatic and chromatographic studies. Investigation of the livers indicated that some hydrolytic enzymes were stimulated with simultaneous decrease of glycogen, lipid and RNA level. [Ad.Hu.]

See also abstract no. 995.

9. Other methods

1240 – Derivation of the general equation for redoxokinetic potential (in English). S. K. Rangarajan (Alagappa Chettiar College of Engineering and Technology, Karaikudi, India). *J. Electroanal. Chem.*, 1 (1959/1960) 396.
A formal derivation of the general expression for the redoxokinetic potential is given. The equations of Barker and Oldham are shown to be particular cases of the general equation. [Author]

1241 – A simple extrapolation method in connection with the measurement of dielectric losses (in German). F. Oehme and M. Feinauer (Institut z. Entwicklung chem.-physik. Analysenmethoden, Weilheim/Obb., Deutschland). *Mitt. Inst. Entwicklung chem.-physik. Analysenmeth., Weilheim/Obb.*, 1 (1961) 17.
Im Zusammenhang mit der Untersuchung der oxydativen Ölalterung auf der Grundlage dielek-

trischer Messungen interessiert die Gleichstromleitfähigkeit. Diese unterliegt bei der Messung zahlreichen Fehlermöglichkeiten, weshalb von der Möglichkeit, die Leitfähigkeit aus dem dielektrischen Verlustfaktor tan σ zu bestimmen, Gebrauch gemacht wird. Nach Messung von tan σ bei verschiedenen niederen Frequenz wird die Leitfähigkeit berechnet und nach einer von A. Sippel (*Angew. Chem.*, 71 (1959) 334) angegebenen Methode auf die Frequenz 0, das heisst den Gleichstromwert, extrapoliert. [Fr.Oe.]

1242 – Theory of chronopotentiometry with cylindrical electrodes. I. The quinone–hydroquinone reaction at platinum and gold wire electrodes. Dennis G. Peters and James J. Lingane (Department of Chemistry, Harvard University, Cambridge, Mass., U.S.A.). *J. Electroanal. Chem.*, 2 (1961) 1.

The theoretical relation for the chronopotentiometric "transition time constant" $ir^{1/2}C_i$ for cylindrically symmetrical diffusion to a wire electrode has been shown to be

$$\frac{i\tau^{1/2}}{C_i} = \frac{\dfrac{\pi^{1/2} n F A D^{1/2}}{2}}{\left[\dfrac{1 - \pi^{1/2} D^{1/2} \tau^{1/2}}{4r_0} + \dfrac{D\tau}{4r_0^2} - \dfrac{3\pi^{1/2} D^{3/2} r^{3/2}}{32 r_0^3} \cdots\right]}$$

where τ is the transition time (sec), i is the constant current (A), C_i is the concentration in the body of the solution of the electroactive substance (moles/cm^3), D is the diffusion coefficient (cm^2/sec), 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 electrode (cm^2) and r_0 is the radius of the electrode (cm). The validity of this equation has been demonstrated with data obtained for the reduction of quinone in 1 M sulfuric acid.

In this relation the current i is only that resulting from the reaction of the electroactive substance, and if extraneous reactions occur the pertinent value of i is smaller than the observed current $i_{obs.}$. In anodic chronopotentiometry the chief extraneous reaction is oxidation of the gold or platinum electrode itself.

From data for the oxidation of oxalic acid and hydroquinone, it has been found empirically that $i \simeq i_{obs.} - (Q/\tau)$, where τ is the total transition time in an actual trial and Q is the quantity of electricity corresponding to the extraneous reaction. As a first approximation Q can be evaluated by measuring the transition time with the supporting electrolyte alone. This simple empirical correction is remarkably effective even down to concentrations so small that Q/τ is of the order of $\frac{1}{2} i_{obs.}$. [Authors]

1243 – Theory of chronopotentiometry with cylindrical electrodes. II. Application of theoretical transition time relation in reduction of ferric iron and hydrogen ion. James J. Lingane (Department of Chemistry, Harvard University, Cambridge, Mass., U.S.A.). *J. Electroanal. Chem.*, 2 (1961) 46.

The theoretical equation for the transition time, based on cylindrically symmetrical diffusion as the sole means of mass transfer, has been further verified by studying the reduction of iron(III) to the (II) state and the reduction of hydrogen ion to hydrogen at a platinum wire electrode. Transition time data for ferric iron reduction agree excellently with the theoretical values over a wide range of current densities. Agreement between observed and theoretical transition times in the reduction of hydrogen ion has also been demonstrated, but, because of the extraordinarily large diffusion coefficient of hydrogen ion, an awkwardly large number of terms in the series expansion of the theoretical equation is necessary at relatively large transition times. Empirically it was found that $ir^{1/2}C$ is very nearly a linear function of $r^{1/2}$, and this simple empirical relation is more convenient than the theoretical equation in practical applications of chronopotentiometry. [Author]

1244 – Dielectric measurements for structure determinations and quantitative analysis (in English). Friedrich Oehme (Institut z. Entwicklung chem.-physik. Analysenmethoden, Weilheim/Obb., Deutschland). *J. Electroanal. Chem.*, 1 (1959/1960) 181.

After briefly considering the physical definition of dielectric values, the practical possibility of structure determination and quantitative analysis using these values is discussed and the close correlation between the two lines of work examined.

In particular it is shown that the quasi-static dielectric constant (*D.K.*) is directly related to the molecular dipole moment and so is influenced correspondingly by changes in chemical structure. Since this constant may be estimated with approximately the same sensitivity as the refractive

index by use of an ordinary refractometer, while it embraces an essentially wider numerical range, it is especially suitable for both purity control and quantitative analysis of binary and pseudo-binary systems. Ternary and higher systems cannot be satisfactorily analysed by *D.K.* measurements alone. In such cases, measurement of *D.K.* in combination with measurement of other quantities may be used, or else the components to be measured may be selectively separated from the system. A special example of the application of *D.K.* measurements is the estimation of water in various substances.

Measurements in the dispersion region have hitherto chiefly been used for structural investigations and are specifically characterised by the fact that they are altered by variations in molecular quantities such as "internal viscosity" and "molecular radius". The conclusions of such measurements, together with the theory of Eyring, lead to thermodynamic relationships. [Author]

1245 – Electrolytic reoxidation after current reversal in chronopotentiometry (in English). Claudio Furlani and Giorgio Morpurgo (Chemical Institute, University of Trieste, Italy). *J. Electroanal. Chem.*, 1 (1959/1960) 351.

The authors present a theoretical treatment of the problem of determining the transition time of the reoxidation processes which occur after current reversal at the end of an electrolytic reduction in chronopotentiometry, when the reduced form is unstable and is being decomposed according to a first-order reaction. Assuming semi-infinite linear diffusion and equal diffusion coefficients for the reduced and the oxidized form a very simple relation is obtained, connecting the transition times of reduction and of reoxidation with the rate constant of the reaction, independently of all other experimental conditions. The validity of this relation has been tested in the case of the reduction and subsequent reoxidation of Fe^{3+} in alkaline triethanolamine solution, in the presence of hydroxylamine which acts as a regenerating agent for the oxidized form. [Authors]

1246 – Voltammetric membrane electrodes. III. Controlled current voltammetry. R. C. Bowers, G. Ward, C. M. Wilson and D. D. DeFord (Department of Chemistry, Northwestern University, Evanston, Ill., U.S.A.). *J. Phys. Chem.*, 65 (1961) 672.

The rigid structure of the membrane minimizes stirring and convection effects, therefore the voltammetric membrane electrodes are well suited for controlled current voltammetry. Expressions for transition times for constant current chronopotentiometry and linear current-scan chronopotentiometry under conditions of linear finite diffusion are derived and it is shown that these reduce to those for infinite diffusion at short transition times. [D.S.Ru.]

1247 – Determining strontium-90 in soil by electrodialysis and an ion-exchange method (in English). E. R. Graham (Science Laboratory, Los Alamos, N. Mex., U.S.A.). *Soil Sci.*, 88 (1959) 11–15.

A 5 g sample is placed in a filter-paper sac, immersed in water and electrodialysed for 12 h at 100 V. A platinum foil anode and a stainless steel cathode are used. The contents of the bag are washed with 1 *M* HCl. The liquid and washings are made 1% in EDTA and the pH is brought to 10 with NaOH. After complete chelation of Ca and Mg is achieved the solution is brought to pH 5.5 to liberate ^{90}Sr and passed through a column of Dowex 50–X12 as the chloride. The existing ^{90}Y is eluted with 500 ml solution containing 1% citric acid and 0.75% EDTA (pH 5) at a rate of 8 ml/sq. cm/min. The completion of this elution is taken as zero time. After a given time (48 h or more) the newly formed ^{90}Y is eluted at the same rate with 50 ml 5% citric acid (pH 2) followed by 350 ml 5% acid adjusted to pH 3.8. The combined eluates are evaporated to half volume, treated with 30 mg Y as carrier and with sufficient KF, to 3 *M* concentration. The precipitate is collected, washed dried, weighed and counted. The estimation of ^{90}Sr activity is taken from a suitable graph of time versus ^{90}Y activity. [Gio.Ser.]

1248 – Electric properties of systems formed by tetravalent titanium and ethers of trichloroacetic acid. (in Russian). O. A. Osipov and Yu. A. Lisenko (State University, Rostov on Don, U.S.S.R.). *Zhur. Obscheĭ Khim.*, 30 (1960) 3866–3869.

The dielectric constant, polarisation and dipole moment of tetravalent titanium solutions in ethyl trichloroacetate, *n*-butyltrichloroacetate, *iso*butyltrichloroacetate and *iso*amyltrichloracetate have been measured. It has been found that at 20° strongly dissociated compounds of equimolecular composition are formed. Results are tabulated. [Ot.So.]

1249 – Application of anodic chrono-amperometry to trace determination of triphenyl tin acetate (in French). Paul Nangniot and Pierre H. Martens (Institut Supérieur Agronomique de l'Etat, Gembloux, Belgique). *Anal. Chim. Acta*, 24 (1961) 276–279.

Using a hanging drop mercury electrode the determination of triphenyl tin acetate as fungicide residues on vegetable matter has been made. After mineralisation of the material, and solution in 5 *N* hydrochloric acid, the solution is transferred to the polarographic cell, deaerated, and electro-

lysed at —0.7 V *vs.* a saturated silver electrode for 5 min. The anodic dissolution wave between —0.7 and —0.1 V *vs.* a saturated silver electrode is then recorded. The accuracy is higher than in conventional polarography. With longer pre-electrolysis times and stirred solutions, it is possible to determine 0.2 μg of triphenyl tin acetate in 25 ml. [Ph.Me.]

1250 – Electrochemical determination of submicrogram quantities of Mo. H. E. Palmer (General Electric Co., Hanford Atomic Products Operation, Richland, Wash., U.S.A.). *Nuclear Sci. Abstr.*, 15 (1961) 19, *Abstr. No.* 128. [Red.]

1251 – Chronopotentiometric determinations at solid electrodes: determination of manganese in steels. Donald G. Davis and John Ganchoff (Georgia Institute of Technology, Atlanta, Ga., U.S.A.). *J. Electroanal. Chem.*, 1 (1959/1960) 248.
A technique has been developed for the accurate determination of several substances by means of chronopotentiometry. This method can be used even when the Sand equation is not obeyed due to kinetic interferences. Various alloys have been analyzed for manganese using this technique. [Authors]

1252 – Chronopotentiometry with platinum and gold anodes. II Oxidation of oxalic acid. James J. Lingane (Department of Chemistry, Harvard University, Cambridge, Mass., U.S.A.). *J. Electroanal. Chem.*, 1 (1959/1960) 379.
The oxidation of oxalic acid to carbon dioxide and hydrogen ion at platinum and gold wire anodes has been studied by the chronopotentiometric technique, with particular attention to the effects produced by oxidation of the electrodes themselves. The prior presence of a film of platinum oxides on a platinum anode inhibits the oxidation of oxalic acid so completely that no chronopotentiometric wave is observed. With orginally clean (reduced) electrodes a very well defined chronopotentiogram for the oxidation of oxalic acid is produced and the transition time is governed by the rate of mass transfer (by diffusion) rather than by kinetic factors. However, oxidation of the electrodes themselves increases the transition time because it decreases the current efficiency for oxidation of oxalic acid. It was discovered that the corrected current for the oxidation of oxalic acid is given very simply by $i_{corr.} = i_{obs.} - Q/\tau$, where $i_{obs.}$ is the observed current, τ is the total transition time, and Q is the quantity of electricity required to oxidize the electrode to the potential at which the transition time was measured. This study has also provided information on the effect of the cylindricity of the diffusion field at wire electrodes on the rate of diffusive mass transfer. [Author]

1253 – Radio-frequency dielectric dispersion in solid ethyl stearate. D. W. Davidson (Applied Chemistry Division, National Research Council, Ottawa, Canada). *Can. J. Chem.*, 39 (1961) 1321.
A study was made of the dielectric properties of solid ethyl stearate between —100° and the melting point at frequencies between 100 cycles/sec and 80 Mc/sec. The circular arc locus lying within this frequency range in the β form consists of a time-dependent and time-independent part. It is more likely to arise from rotational disorder of tilted molecules than from regions of vertically stacked molecules. [D.S.Ru.]

1254 – The dipole moment of norbornylene. Use of the IBM 650 computer for dipole moment calculations. Norman L. Allinger and Janet Allinger (Department of Chemistry, Wayne State University, Detroit, Mich., U.S.A.). *J. Org. Chem.*, 24 (1959) 1613–1614.
Norbornylene (bicyclo [2.2.1.] hept-2-ene) contains a "strained" olefinic linkage; in order to determine what effect such strain exerts upon the dipole moment, the authors have measured the moment in heptane solution. The value observed is 0.40 *D*; the effect of the strain on the dipole moment is not important. To speed the dipole moment calculation, an IBM automatic computer has been used. The operation of putting the experimental data into the punched cards takes only 15 min and the computer reads the program and data cards and does all the calculations in about 3 min. [Su.Mo.Ce.]

1255 – Dielectric relaxation of aqueous glycine solutions at 3.2 centimeter wave length. Oscar Sandus and Betty B. Lubitz (Department of Electrical Engineering, The Radiation Laboratory, The University of Michigan, Ann Arbor, Mich., U.S.A.). *J. Phys. Chem.*, 65 (1961) 881.
The dielectric constants and the dielectric loss factors of water and aquous glycine solutions (0.25–1.0 *M*) are given at 20–50° at 3.2 cm wave length. The Oncley equation for high frequency dielectric constants of proteins is not consistent with this data or data at a lower frequency. The critical wave length values are in best agreement with those of Bateman and Potapenko. Thermodynamic activation functions were obtained from the critical wave lengths. [D.S.Ru.]

1256 – Electric moment of 3-ethyl-3-methyl glutarimide. Alexander I. Popov and Roger D. Holm (Department of Chemistry, Northern Illinois University, DeKalb, Ill., U.S.A.). *J. Phys. Chem.*, 65 (1961) 774.
The electric moment of 3-ethyl-3-methylglutarimide in benzene solution was found to be 2.84 D. The estimates of bond moments in this compound are inadequate — the H-N bond moment appears to be smaller than commonly assumed. [D.S.Ru.]

1257 – Titrages des chlorures de sulphonyle, sulfinyle et sulfényle par le sulfure de sodium (en français). W. Walisch, D. F. Hertel and M. R. F. Ashworth (Institut de chimie organique, Section analytique, Université de la Sarre, Sarrebruck, Allemagne). *Chimie Anal.*, 43 (1961) 234.
Le point équivalent du titrage de différents chlorures de sulfonyle, sulfinyle, et sulfényle par le sulfure de sodium est déterminé soit par l'apparition d'une coloration jaune(polysulfure) soit par une méthode électrochimique indicatrice, la polaro-voltamétrie, (potentiomètrie à courant imposé sensiblement constant). Le dosage est réalisé en milieu eau–acétone (40–90% d'acétone) en présence de chlorure de sodium pour rendre le milieu conducteur. Les autres dosent les substances suivantes: chlorure de méthane-sulfonyle; chlorure de benzène-sulfonyle; chlorure de *p*-toluène-sulfonyle; chlorure de *p*-chlorobenzène-sulfonyle; chlorure de *p*-bromobenzène-sulfonyle; chlorure de *p*-méthoxybenzène-sulfonyle; chlorure de pipéridine N-sulfonyle; chlorure de naphtalène-1-sulfonyle; chlorure de naphtalène-2-sulfonyle; chlorure de tétraline-sulfonyle; chlorure d'anthraquinone-1-sulfonyle; dichlorure de benzène-1-3-disulfonyle; chlorure de chlorusulfonyle acétyle-2-benzène-sulfonyle. Dans le cas du chlorure de *p*-toluène sulfonyle, on dose 70 mg de produit à 0.3% près. Les auteurs signalement que les solutions 0.001 *M* peuvent encore être titrées d'une façon satisfaisante. Les sulfonates et sulfinates de sodium, les acides chlorhydrique, sulfonique et sulfinique préalablement neutralisés, ne genent pas le titrage des chlorures de sulfonyle.
Les chlorures de sulfinyle et de sulfényle ne fournissent pas de résultats satisfaisantes, exception faite pour le chlorure de trichlorométhyle-sulfényle, CCl_3—S—Cl. [Bad.Lam.]

10. Related topics

1258 – Streaming potential of metal–aqueous electrolyte solution systems and catalytic activity of metals (in Polish). Z. Sokalsky (Department of Physical Chemistry, Politechnika, Gliwice, Poland). *Roczniki Chem.*, 35 (1961) 649.
Electrokinetic potential measurements were performed for the system metal–aqueous electrolyte solution. For given dynamic conditions a mathematical equation was derived expressing the relation between the concentration of monovalent cations in a solution of a given electrolyte and the elektrokinetic potential. [Ad.Hu.]

1259 – Influence of alkali metal cations on hydrogen overvoltage on mercury in acid solutions (in Russian). E. A. Maznitshenko, B. B. Damaskin and Z. A. Iofa (M. V. Lomonosov State University, Moscow, U.S.S.R.). *Doklady Akad. Nauk S.S.S.R.*, 138 (1961) 1377–1380.
Hydrogen overvoltage has been measured on the mercury drop electrode in 0.01 and 0.001 *N* HCl solutions, both pure and containing additions of Li, Na, K, Rb and Cs chlorides. In the range of current densities investigated ($10^{-4.8}$–$10^{-3.5}$ A/cm^2) linear dependence of overvoltate on the value log *i* was found. The slope of the lines is 0.110–0.111 V for 0.33 *N* salt concentration, ando. 116 V for 1 *N* solutions. Resulting overvoltage values are tabulated. [Ot.So.]

1260 – The mechanism of the electrodeposition of titanium from fused salts. Y. A. Menzies, D. L. Hill, L. Young and J. O'M. Bockris (Chemistry Department, Imperial College, London, Gt. Britain). *J. Electroanal. Chem.*, 1 (1959/1960) 161.
(1) An outline is given of original experimental methods for making electrode-kinetic measurements in fused salts, when the metal is easily attacked by oxygen-containing species.
(2) Experimental conditions are reported which give rise to (a) dendritric and (b) spongy titanium.
(3) Polarographic evidence indicates that when the conditions of deposition are such that dendrites are obtained, a limiting current due to Ti-containing ions is observable, but when conditions are such that spongy Ti is obtained, the only polarographic wave observable is that due to alkali ions.
(4) A mechanism for the formation of spongy and dendritic Ti is suggested.
(5) On the basis of the mechanism, conditions are suggested which tend to give rise to high purity, dendritic electro-deposited transition metals. [Authors]

1261 – Migration of toxic substances from lead–tin packings used in the cosmetics industry (in Polish). B. Legatowa (Department of Food Research, State Department of Hygiene, Warsaw, Poland). *Roczniki Państ. Zakladu Hig.*, 12 (1961) 329–338.

To determine the degree of lead and tin corrosion from metal packings experiments were performed in which the metal content was determined in cosmetics kept in metal tubes. The mechanism of corrosion was investigated with model experiments consisting of measurements of electric tension of cells composed of lead and tin electrodes dipped in the cosmetics studied. It was stated that for acidic and alkaline cosmetics the presence of tin plates prevents corrosion of lead, but for neutral and slightly alkaline preparations the presence of lead plating with tin inhibits dissolution of lead as long as the plating is sufficiently tight. When small spots of exposed tin exist, rapid electrochemical corrosion is due to the presence of significant amounts of lead in the preparations.

[Ad.Hu.]

1262 – Electrodepostion of nickel–iron–tungsten ternary alloys from the pyrophosphate bath (in English). K. I. Vasu and T. L. Ramachar (Indian Institute of Science, Bangalore, India). *J. Sci. Ind. Research (India)*, 20 B (1961) 241.

The pyrophosphate bath has been used for the electrodeposition of ternary alloys of nickel, iron and tungsten. Optimum conditions have been established for obtaining satisfactory alloy plates with 14–75% nickel, 10–53% iron and 11–48% tungsten. [R.S.Sa.]

1263 – Kolbe's reaction of higher fatty acids. II. Electrolysis of lauric acid by a pulsating current with an artificial graphite anode (in English). R. Matsuda, T. Hisano and D. Kubota (Faculty of Engineering, Tokushima University, Tokushima, Japan). *Bull. Chem. Soc. Japan*, 34 (1961) 649.

The electrolysis of lauric acid was studied at graphite, lead, tantalum, molybdenum, tungsten and iron anodes. No Kolbe reaction occurred with direct current; pulsating current (half-wave rectified sinusoidal 60 cycles/sec), however, produced some Kolbe reaction at a graphite electrode (but not at electrodes of the other materials mentioned). The current efficiency increased (from *ca.* 16% to *ca.* 28%) with increasing current density (0.2–0.8 A/cm^2) but decreased with increasing alkalinity of the solution (from 40% to $<$ 10% as the hydroxide content was increased five-fold).

[H.H.Ba.]

1264 – The dipole moments of some heptafulvene derivatives (in English). Masumi Yamakawa and others (Chemistry Department, Nagoya University, Chikusa, Nagoya, Japan). *J. Am. Chem. Soc.*, 82 (1960) 5665.

The authors have measured the dielectric constants and densities of benzene or dioxane solutions of heptafulvene-8,8-dinitrile(I), 8-ethoxycarbonylheptafulvene-8-nitrile(II), tropylmalononitrile (III), ethyl tropylcyanoacetate(IV), diethyl tropylmalonate(V), ditropylmalononitrile(VI), and ethyl ditropylcyanoacetate(VII). These data were used to calculate the dipole moments for these compounds. The results obtained were: (I) 7.49, (II) 4.40, (III) 4.12, (IV) 3.56, (V) 2.44, (VI) 4.35, and (VII) 3.35. Calculation of D for heptafulvene and 7-methylcycloheptatriene from the above values yielded 3.07 and 0.13, respectively. The charge distribution in these molecules is discussed.

[R.W.Mur.]

CONTENTS

Original papers

Le comportement polarographique de l'ion chromate
I. Élucidation du mécanisme réactionnel et étude de l'influence de l'électrolyte-support
par J. J. TONDEUR, A. DOMBRET ET L. GIERST (Bruxelles) 225

A polarographic study of some complexes of molybdenum
by E. W. ZAHNOW AND R. J. ROBINSON (Washington) 263

Anwendungen der Aminoverbindungen in der Polarographie anorganischer Stoffe.
XII. Die Bestimmung von Kadmium, Blei und Thallium in Indium
von J. DOLEŽAL, V. PETRUS AND J. ZÝKA (Prag) 274

Potentiometric study of the oxidation of trivalent molybdenum by lead tetraacetate
by A. BERKA, J. DOLEŽAL, L. NĚMEC AND J. ZÝKA (Prague) 278

Short communications

Separation of inorganic ions in fused salts by electrophoresis on glass fiber paper
by G. ALBERTI, G. GRASSINI AND R. TRUCCO (Rome) 283

Differential arrangement of antimony electrodes for pH measurement
by A. E. SIMCHEN (Tel Aviv) 286

Book Reviews 288

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