

Journal of

# ELECTROANALYTICAL CHEMISTRY

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

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# mass spectrometry

## and its use in organic chemistry

by

**J. H. BEYNON**

*Research Physicist, Imperial Chemical Industries, Manchester (England)*

The author has in this book summarized his experiences in applying mass spectrometry in the chemical industry. The application of the techniques to the identification of unknown organic substances and to related chemical problems forms the central theme. Instrument design, experimental techniques, as well as applications of wider relevance are also discussed. An important section appended to the text consists of a long compilation of mass and abundance values for various atomic combinations, which will be of great value in identificational work.

**7 x 10"    viii + 638 pages    185 illustrations    2213 refs.    1960**

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## I. THEORETISCHE BETRACHTUNGEN

Die Leitfähigkeit fester und flüssiger Körper lässt sich hauptsächlich auf zwei ganz verschiedene Mechanismen zurückführen, wobei als wesentliches Unterscheidungs-

TABELLE I

ZUSAMMENSTELLUNG DER WICHTIGSTEN EIGENSCHAFTEN DER VERSCHIEDENEN ARTEN DER CHEMISCHEN BINDUNG

<i>Metallische Bindung</i>	<i>Valenzbindung</i>	
Keine exakten stöchiometrischen Gesetzmässigkeiten	exakte stöchiometrische Gesetzmässigkeiten Homöopolare- oder unpolare (kovalente) Bindung	Atom-Bindung polare (elektrovalente) Bindung heteropolare- oder Ionen-Bindung
Kein Bindungsmoment angebbbar	Bindungsmoment = 0	endliches Bindungsmoment
Gitterbausteine Kationen, bindende Elektronen mit Eigenschaften eines Elektronengases	ungeladene Gitterbausteine (Atom- oder Molekülgitter)	geladene Gitterbausteine (Ionengitter)
Elektronen-Leitfähigkeit	keine unmittelbare Ionenleitfähigkeit, Verhalten als potentielle Elektrolyte	Ionen-Leitfähigkeit
Makroskopische Eigenschaften, wie Härte, Schmelzpunkt, je nach Stellung im periodischen System	makroskopische Eigenschaften, wie Härte, Schmelzpunkt, stark unterschiedlich	makroskopische Eigenschaften sehr ähnlich
Metalle, intermetallische Verbindungen und Legierungen	zweiatomige Gase, (H <sub>2</sub> , N <sub>2</sub> ) Kohlenwasserstoffe, diamantähnliche Substanzen	Chlorwasserstoff, mit funktionellen Gruppen substituierte Kohlenwasserstoffe anorganische Salze

merkmal die Art der chemischen Bindung herangezogen werden kann, wie Tabelle I veranschaulicht.

Aus dieser Zusammenstellung geht hervor, dass die *Elektronenleitfähigkeit* ein wesentliches Merkmal der metallischen Bindung ist. Dabei besteht ein enger Zusammenhang mit der Elektronenbesetzung der einzelnen Schalen und ihren energetischen Zuständen. Bekanntlich erfolgt die Elektronenbesetzung der Schalen bei Elementen steigender Ordnungszahl nach dem Pauli-Prinzip mit Elektronenpaaren antiparallelen Spins. Sind dabei alle Energiebänder mit Elektronen aufgefüllt worden, befindet sich

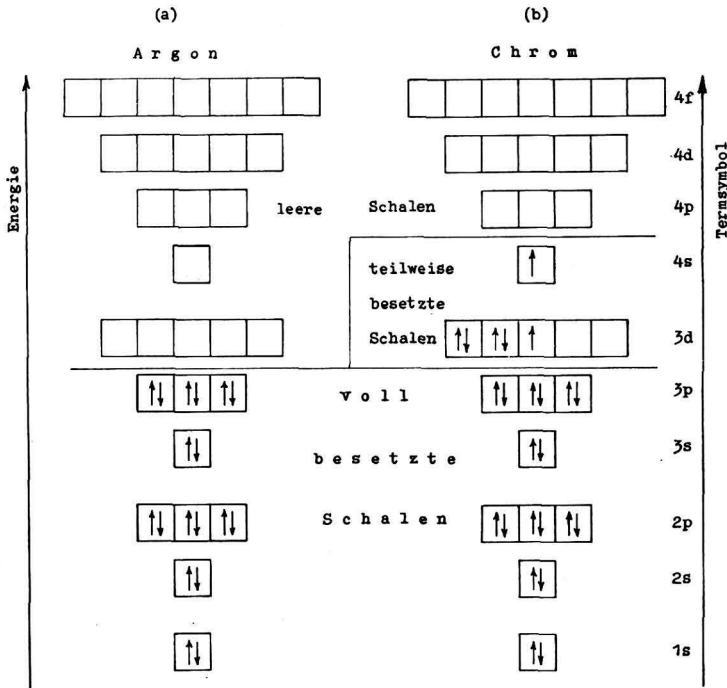


Fig. 1. Vergleich der Besetzung der einzelnen Schalen mit Elektronen: (a), bei dem Edelgas Argon; (b), bei dem Metall Chrom.

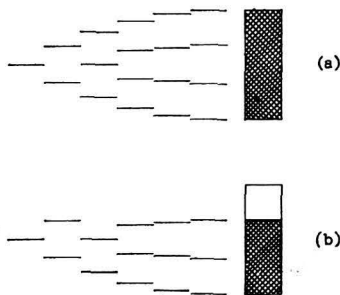


Fig. 2. Auffüllen eines Energiebandes eines Elementes mit Elektronen: (a), voll besetztes Energieband = Nichtleiter; (b), teilweise besetztes Energieband = Elektronenleiter.

das nächst höhere Energieband in einem Zustand wesentlich grösseren Energieinhaltes. Unter Normalbedingungen kann folglich kein Elektronenübergang zwischen den beiden Bändern stattfinden und das fragliche Element ist ein Nichtleiter (Fig. 1(a)).

Ist dagegen ein Energieband nur teilweise mit Elektronen besetzt, gibt es zahlreiche Zustände von Elektronen, welche sich vom Grundzustand nur um einen geringen Energiebetrag unterscheiden und es genügt bereits ein schwaches äusseres elektrisches Feld, um eine Elektronenbewegung unter „Anheben“ der Elektronen auf einen etwas höheren Energiezustand auszulösen. Es tritt in diesem Falle Elektronenleitfähigkeit auf (Fig. 1(b)). Fig. 1 und 2 veranschaulichen an Hand schematisierter Darstellungen diese Zusammenhänge nochmals.

Interessanterweise kann Elektronenleitfähigkeit in Sonderfällen auch bei organischen Molekülen auftreten. Es handelt sich dabei um hochkondensierte aromatische Systeme, welche reich an  $\pi$ -Elektronen sind<sup>1,2</sup>. Auch die lichtelektrische Leitfähigkeit verschiedener anorganischer<sup>3</sup> und organischer Verbindungen<sup>4,5</sup> steht in engem Zusammenhang mit diesen Erscheinungen.

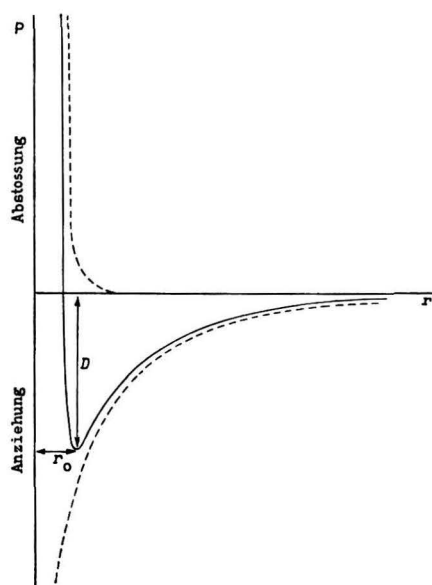


Fig. 3. Abhängigkeit der potentiellen Energie zweier Ionen entgegengesetzter Ladung von ihrem Abstand  $r$ .  $D$  = Dissoziationsarbeit,  $r_0$  = stabile Lage kleinster Energie.

Ganz andere Verhältnisse liegen dagegen vor, wenn es sich um Stoffe mit *Ionenleitfähigkeit* handelt. Diese tritt stets bei Substanzen mit heteropolarer Bindung auf, welche als Ionengitter kristallisieren. Ein Ionengitter kann bekanntermassen als Kombination eines Teilgitters aus Anionen und Kationen aufgefasst werden. Bei Unterschreiten des Erstarrungspunktes der Schmelze eines Ionengitterkristalls sind die beiden Ionenarten bereits recht fest an bestimmte Plätze gebunden, von welchen sie zum Beispiel in Abhängigkeit von der Temperatur oder unter Einfluss eines polarisierenden elektrischen Feldes Verschiebungen in nur engen Grenzen erfahren können.

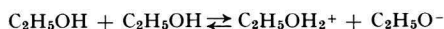
Wird die potentielle Energie  $P$  zweier Ionen entgegengesetzter Ladung in Abhängigkeit von ihrem gegenseitigen Abstand  $r$  graphisch ausgewertet, so ergibt sich eine in Fig. 3 dargestellte Abhängigkeit.

Das bei diesen Untersuchungen beweglich gedachte Ion befindet sich in einem Potentialtopf kleinsten Energieinhaltes. Die Tiefe des Topfes wird dabei durch die Dissoziationsarbeit  $D$ , welche zur völligen Trennung der beiden Ionen aufgewandt werden muss, gekennzeichnet. Die erforderliche Dissoziationsarbeit  $D$  kann nun beispielsweise durch Wärmezufuhr geleistet werden, was sich in dem scharfen Schmelzen von Ionengitterkristallen und der in der Schmelze auftretenden Ionenleitfähigkeit zu erkennen gibt. Von besonderer Bedeutung für die Elektrolytforschung ist dabei, dass  $D$  im Falle von Lösungen wesentlich von der Dielektrizitätskonstanten (DK) abhängig ist. So nimmt für Lösungsmittel hoher DK die Dissoziationsarbeit sehr stark ab — für den Fall des Wassers mit einer DK  $\epsilon = 80$  im Vergleich zum Wert  $\epsilon = 1$  des Vakuums um etwa zwei Zehnerpotenzen. Das bedeutet, dass in derartigen Lösungsmitteln bereits bei Raumtemperatur weitgehende Dissoziation zustande kommen kann.

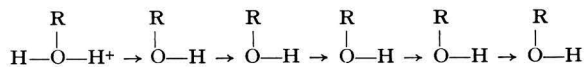
Diese zunächst für Elektrolyte mit heteropolarer Bindung gültigen Gesetzmässigkeiten haben auch für das Leitfähigkeitsverhalten flüssiger Nichtelektrolyte höherer DK ( $\epsilon > 10$ ) Gültigkeit. Die später noch näher zu beschreibenden flüssigen Nichtelektrolyte (hier interessieren speziell Lösungsmittel) enthalten sehr häufig Elektrolytspuren, welche durch das Auftreten elektrolytischer Leitfähigkeit die Leitfähigkeit der Lösungsmittel bestimmen, ohne dass es sich dabei um eine echte Eigenleitfähigkeit handeln würde.

Es gibt nun aber auch Fälle, wo eine echte und nicht durch Verunreinigungen bedingte Eigenleitfähigkeit organischer Flüssigkeiten zustande kommen kann. Im allgemeinen geschieht das durch eine Wechselwirkung zweier neutraler Moleküle im Sinne einer Donator-Akzeptor-Beziehung miteinander, wobei ein Ladungsaustausch zu verzeichnen ist, sodass Ionen entstehen.

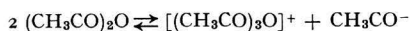
Nach der Art des den Ladungsaustausch bedingenden Molekülteiles kann zwischen einer *Prototropie* und einer *Ionotropie* unterschieden werden. Prototropie tritt zum Beispiel bei aliphatischen Alkoholen auf:



Neben dieser Bildung von Organo-Ionen kann ausserdem noch eine Protonenwanderung über eine Assoziatkette von Alkoholmolekülen auftreten und zu einer *Protonenbrückenleitfähigkeit* führen:



Bei einer Ionotropie kann der Ladungstransport von grösseren Molekülbruchstücken übernommen werden, wie das beim Essigsäureanhydrid zutrifft<sup>6</sup>:



Prototropie kann im Falle der Anwesenheit von geeigneten verunreinigenden Komponenten auch mit diesen ausgebildet werden. Stellt die verunreinigende Komponente Wasser dar, kann dieses — als Sonderfall der Ionotropie — wieder eine prototrope Wechselwirkung mit der Grundkomponente eingehen.



In völliger Analogie zu den klassischen Elektrolyten erfolgt in all diesen Fällen der Ladungstransport durch Organo-Ionen. Definitionsgemäss unterscheidet Fuoss die echten Elektrolyte als *Ionophore* von den zuletzt betrachteten Fällen, welche er *Ionogene* nennt. Kortüm spricht hier dagegen von *potentiellen Elektrolyten*. Schliesslich kann noch ein ganz anderer Vorgang zum Auftreten von Ladungsträgern, die im elektrischen Feld wandern, führen. Das trifft für binäre dispergierte Systeme zu, wenn dispergierte Substanz und Dispersionsmittel eine unterschiedliche DK und verschiedene Leitfähigkeit aufweisen. Es handelt sich dabei im Gegensatz zu den bisherigen Systemen um inhomogene Mischungen (wobei die Inhomogenität bis zur kolloiden Verteilung gehen kann, sodass das System äusserlich zunächst homogen erscheint). Nach der Coehn'schen Regel kommt es bei binären, heterogenen Systemen zu einer Ladungstrennung in dem Sinne, dass die Phase mit der höheren DK eine positive, die mit der niederen DK eine negative Ladung annimmt. Bei einem Kohlenwasserstofföl dispergierten Wassertröpfchen bedeutet dies, dass die Tröpfchen eine positive Ladung in dem negativ geladenen Dispersionsmittel aufweisen. Damit sind die Wassertröpfchen aber wie Quasi-Ionen in der Lage, im elektrischen Feld zu wandern (was praktisch tatsächlich so weit geht, dass an der Kathode bei Messungen mit Gleichspannung die Tröpfchen entladen und als Wasserfilm abgeschieden werden; der fliessende Strom als Mass für die Leitfähigkeit ist zeitlich somit inkonstant!).

## 2. MESSTECHNISCHE ANGABEN

Die spezifische Leitfähigkeit von Nichtelektrolyt-Systemen der betrachteten Art liegt wesentlich unter der von (wässrigen) Elektrolyt-Lösungen. Der interessierende Leitfähigkeitsbereich erstreckt sich von etwa  $10^{-6}$  bis  $10^{-14}$   $\text{Ohm}^{-1}\text{cm}^{-1}$ . Die in der Elektrochemie der Elektrolyte üblichen Messschaltungen, welche fast immer auf der klassischen Wheatstone-Brücke aufbauen, eignen sich zur Bestimmung so kleiner Leitfähigkeiten nicht mehr. Der zu messende Widerstand  $R$  einer die Probe aufnehmenden Messzelle mit der Zellenkonstante  $k$  berechnet sich bekanntermassen für eine Probe mit der spezifischen Leitfähigkeit  $\kappa$  zu  $R = k/\kappa$ . Selbst wenn die Zellenkonstante  $k = 10^{-2}$   $\text{cm}^{-1}$  beträgt, d.h. wenn eine grosse Elektrodenfläche und ein kleiner Elektrodenabstand gegeben ist, wird für eine Probe mit  $\kappa = 10^{-8}$   $\text{Ohm}^{-1}\text{cm}^{-1}$  der Widerstand  $R = 10^6$   $\text{Ohm}$  (= 1 Meg-Ohm). Für  $\kappa = 10^{-14}$   $\text{Ohm}^{-1}\text{cm}^{-1}$  ergibt sich  $R = 10^{12}$   $\text{Ohm}$  (= 1 Tera-Ohm). Die zu messenden Widerstände liegen also zwischen dem Meg-Ohm- und dem Tera-Ohm-Gebiet.

Messungen in diesem Widerstandsbereich werden nun sehr häufig nach einer sogenannten Spannungsteilerschaltung unter Verwendung von Gleichspannung vorgenommen. Nach Fig. 4 wird dabei die mit der Probe beschickte Messzelle  $R_X$  mit

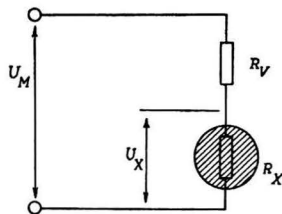


Fig. 4. Prinzip-Schaltung einer Widerstands-Messung nach der Spannungsteiler-Methode (vergl. Gl. (1)).

einem Vorwiderstand  $R_V$  in Reihe geschaltet und an die Messspannung  $U_M$  gelegt. Mit einem Röhrevoltmeter wird der sich über  $R_X$  ergebende Spannungsabfall  $U_X$  gemessen. Der gesuchte Widerstand  $R_X$  der Messzelle folgt dann zu,

$$R_X = R_V U_X / U_M \quad (1)$$

Fig. 5 veranschaulicht die praktische Schaltung eines nach der Spannungsteilerschaltung arbeitenden Gerätes.

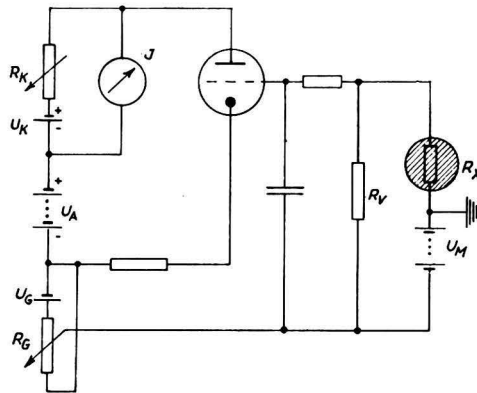


Fig. 5. Schematisierte Schaltung eines nach der Spannungsteiler-Schaltung (Fig. 4) arbeitenden Gleichspannungsgerätes zur Messung hoher Widerstände (Taschen-Megohmmeter MoM 2 T der Fa. W.T.W., Weilheim/Obb.).  $R_X$ , Messzelle mit Probe;  $R_V$ , Vorwiderstand genau bekannter Grösse;  $U_M$ , Messspannung;  $U_A, U_K, U_G$ , Betriebsspannungen der Elektrometerröhre;  $J$ , in Ohm geeichtes Anzeige-Instrument.

Es ist eine bekannte Tatsache, dass bei Messungen mit Gleichspannung eine erhebliche Polarisationsspannung  $U_P$ , welche der Messspannung  $U_M$  entgegengerichtet ist, auftreten kann. Der im aus  $R_V$  und  $R_X$  gebildeten Messkreis fließende Strom wird folglich zu klein ausfallen, da

$$J = \frac{(U_M - U_P)}{R_X} \quad (2)$$

gilt.

Dieses Verhalten kann auch so aufgefasst werden, dass in Reihe zum gesuchten  $R_X$  noch ein weiterer Widerstand, der Polarisationswiderstand  $R_P$ , liegt.

Aus Gl. (2) geht hervor, dass durch die Wahl einer hohen Messspannung  $U_M$  die Polarisationsspannung  $U_P$  vernachlässigbar klein wird. Allerdings muss  $U_M$  dann schon 100 V und mehr betragen, da die Polarisationsspannung  $U_P$  unter Umständen bis zu 20 V ansteigen kann<sup>7</sup>.

Bei Leitfähigkeitsmessungen schlecht leitender Flüssigkeiten ist stets zu kontrollieren, dass der Eigenwiderstand  $R_Z$  der Messzelle um so viel grösser ist als der Widerstand  $R_X$  der mit der Probe gefüllten Zelle, dass er vernachlässigt werden kann. Sind beide Grössen dagegen um weniger als  $10^2$  verschieden, muss eine rechnerische Korrektur, die den Eigenwiderstand der Messzelle berücksichtigt, angebracht werden. Der gesuchte Zellenwiderstand  $R_X$ , welcher unter Verwendung der Zellenkonstante  $k$

zur Berechnung der Leitfähigkeit dient, beträgt dann,

$$R_X = \frac{R_M R_Z}{R_Z - R_M} \quad (3)$$

wenn  $R_M$  der zunächst gemessene Widerstand ist.

Diese Überlegungen gelten unabhängig von der Verwendung von Gleich- oder Wechselstrom-Methoden.

Nur bei Wechselstrom-Methoden ist dagegen zu beachten, dass sich die Widerstandsmesszelle nicht nur wie ein Ohm'scher Widerstand  $R_X$ , sondern zugleich auch wie ein Kondensator von der Kapazität  $C_X$  verhält.

Diese Kapazität  $C_X$  weist einen Blindwiderstand  $X_C$  auf, der sich für eine Kreisfrequenz  $\omega = 2\pi f$  zu  $X_C = 1/\omega C_X$  berechnet. Durch diese Parallelschaltung von  $R_X$  und  $X_C$  wird folglich nicht der gesuchte Zellenwiderstand  $R_X$ , sondern ein resultierender Scheinwiderstand  $Z_{res}$  gemessen (in Ohm), welcher sich zu

$$Z_{res} = \frac{R_X X_C}{\sqrt{R_X^2 + X_C^2}} \quad (4)$$

berechnet. Mit dieser Beziehung lassen sich die gemessenen Werte von  $Z_{res}$  unter Verwendung von  $X_C$  korrigieren.

Wenn  $X_C$  nicht selbst gemessen werden kann, was als Regel gelten dürfte, lässt es sich bei Kenntnis der Zellenkonstante  $k$  und der DK  $\epsilon$  der Probe berechnen. Es gilt dabei

$$X_C = \frac{1,129 \cdot 10^{13} k}{\omega \epsilon} \quad (5)$$

(in Ohm) wenn  $\omega$  wiederum die Kreisfrequenz ist.

Diese Notwendigkeit, Korrekturen anzubringen, entfällt nicht durch den Einbau eines in einem Zweig der verwendeten Messbrücke liegenden, das Abstimm-Minimum verbessernden Kondensators, wie das etwa CRUSE UND STÖHR annehmen<sup>29</sup>. Ausschliesslich bei phaseneempfindlichen Messbrücken wird das gesuchte  $R_X$  in jedem Falle ohne Korrekturnotwendigkeit erhalten<sup>9</sup>. Eine Zusammenstellung über die auftretenden Fehler bringt OEHME<sup>30</sup>.

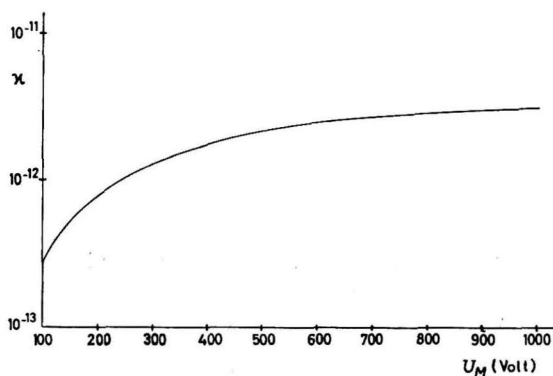


Fig. 6. Abhängigkeit der spezifischen Leitfähigkeit  $\kappa$  eines gealterten Transformatoröles von der an die Messzelle angelegten Spannung  $U_M$ .

Eine weitere Komplikation ist bei heterogenen Systemen zu verzeichnen. Der gemessene Zellenwiderstand  $R_X$  und somit auch die daraus errechnete spezifische Leitfähigkeit  $\kappa$  hängt sowohl von der auf die Probe wirkenden Feldstärke als auch von der Zeit ab, die seit Anlegen des Feldes verstrichen ist. Beide Effekte haben ihre Ursache im Auftreten von Raumladungen und im Zustandekommen einer elektrophoretischen Trennung der Komponenten, wie bereits im vorangegangenen Abschnitt

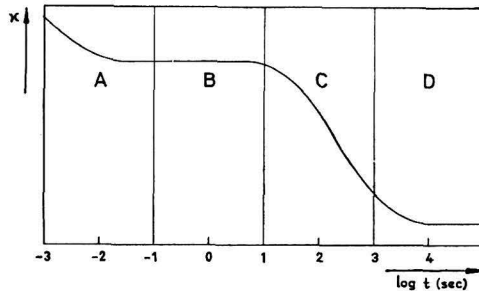


Fig. 7. Abhängigkeit der spezifischen Leitfähigkeit  $\kappa$  eines gealterten Transformatoröles von der nach Anlegen der Messspannung vergangenen Zeit  $t$ . A, Anteil des kapazitiven Blindstromes; B, durch Ionen bedingter Anteil (labil); C, durch Elektrophorese (Ionenverarmung!) verursachtes Übergangsgebiet; D, stabile Endleitfähigkeit.

erwähnt wurde<sup>8</sup>. Die Fig. 6 und 7 vermitteln einen Eindruck über die Grössenordnung der besprochenen Erscheinungen. Der Zeitabhängigkeit der Leitfähigkeit wird nach DIN 53 482 dadurch zu begegnen versucht, dass der Widerstand eine Minute nach Anlegen der Messspannung bestimmt wird. Schwieriger ist es dagegen, den Feldstärke-Effekt auszuschalten. Hierbei spielt nicht nur die äussere, seitens des Messgerätes abgegebene Messspannung  $U_M$  eine Rolle, sondern gemäss der Definition der Feldstärke  $\xi = U_M/d$  mit dem Abstand  $d$  der beiden Elektroden, auch die konstruktive Beschaffenheit der Messzelle. Gerade die zur Berechnung von  $\xi$  erforderlichen Angaben sind aber so gut wie nie in entsprechenden Veröffentlichungen zu finden.

Auch die Bestimmung der Zellenkonstanten  $k$  verdient bei Messungen im Tera-Ohm-Bereich besondere Erwähnung. Der prinzipiell denkbare Weg,  $k$  mit den im Elektrolytbereich üblichen Standard-Lösungen<sup>9</sup> zu bestimmen und die Konstanz von  $k$  auch bei Messungen an Lösungen wesentlich kleinerer Leitfähigkeit vorauszusetzen, hat sich bei grösseren Genauigkeitsansprüchen nicht bewährt. Eine derartige Extrapolation hat nur bei Schutzringmesszellen Sinn, welche jedoch erfahrungsgemäss nur selten verwendet werden.

Der experimentell beste Weg besteht darin, unter Benutzung eines geeigneten Kapazitätsmessgerätes zunächst die „wirksame Kapazität“  $C_W$  der Messzelle zu bestimmen. Das geschieht am einfachsten durch nacheinander vorzunehmende Füllung der Zelle mit zwei Flüssigkeiten genau bekannter DK  $\epsilon_1$  und  $\epsilon_2$  und Messen der sich ergebenden Kapazitäten  $C_1$  und  $C_2$ . Die gesuchte wirksame Kapazität  $C_W$  folgt aus<sup>10</sup>

$$C_W = \frac{C_1 - C_2}{\epsilon_1 - \epsilon_2} \quad (6)$$

Aus dem gemessenen Widerstand  $R_X$  der mit der fraglichen Probe beschickten Messzelle berechnet sich die gesuchte spezifische Leitfähigkeit  $\kappa$  zu

$$\kappa = \frac{8,86 \cdot 10^{-2}}{C_W R_X} \quad (7)$$

Selbst bei sorgfältigster Handhabung haften allen Gleichstrommethoden zur Leitfähigkeitsmessung methodische Fehler an, welche nur schwer eine Messrichtigkeit zulassen, die besser als  $\pm 5\%$  ist. Eine in neuerer Zeit entwickelte 4-Elektroden-Methode leistet zwar hinsichtlich der erreichbaren Messrichtigkeit auch bei Verwendung von Gleichstrom ebenso viel wie die besten Wechselstrom-Methoden. Die Erprobung für Flüssigkeiten sehr kleiner Leitfähigkeit steht jedoch noch aus<sup>11</sup>.

Es hat auch nicht an Versuchen gefehlt, die klassischen Wechselstrom-Messbrücken für Tera-Ohm-Messungen zu modifizieren, wie das z. B. durch Kombination einer phasempfindlichen Wheatstone-Brücke mit einem modulierten Wechselstrom-Anzeigeverstärker geschehen kann.

Trotzdem verbleiben auch hier zellenseitig methodische Fehlermöglichkeiten, die nur bedingt durch das Anbringen von Korrekturen berücksichtigt werden können<sup>9,12</sup>.

Eine von uns erprobte neue Methode unter Verwendung kontaktloser Messzellen ist zwar frei von diesen Fehlermöglichkeiten. Sie lässt sich jedoch aus theoretischen Gründen allenfalls bei einer Messfrequenz von 25 Hz bis herab zu Leitfähigkeiten von  $10^{-10} \text{ Ohm}^{-1} \text{ cm}^{-1}$  einsetzen. Dagegen hat eine von CRUSE UND HUBER beschriebene und als „RC-Titration“ bezeichnete Methode Aussicht, auch für Lösungen kleinerer Leitfähigkeit mit guter Genauigkeit zur Messung herangezogen zu werden<sup>13</sup>.

### 3. PRAKTISCHE ANWENDUNGSBEISPIELE

Die spezifische Leitfähigkeit von Nichtelektrolyten dürfte in vielen Fällen das empfindlichste Reinheitskriterium überhaupt darstellen. Die erheblichen Schwierigkeiten jedoch, welche sich der Schaffung von Substanzen definierter „Leitfähigkeits-Reinheit“ entgegenstellen, haben bewirkt, dass bei Vergleichen der Leistungsfähigkeit verschiedener Methoden zur Reinheitskontrolle, Leitfähigkeitsmessungen im allgemeinen keine Berücksichtigung gefunden haben. Die genannten Schwierigkeiten werden bereits deutlich, wenn man die Angaben verschiedener Bearbeiter über die Leitfähigkeit ein und derselben Verbindung vergleicht. Je nach der gewählten Reinigungsmethode, den durch die Herkunft der Probe bedingten Verunreinigungen und dem bei der Reinigung betriebenen präparativen Aufwand, werden sich unterschiedliche Resultate ergeben. Das drückt sich bei neueren Arbeiten besonders darin aus, dass mit verbesserten Methoden im allgemeinen immer kleiner werdende Werte für die spezifische Leitfähigkeit erhalten werden, ohne dass die gegenwärtigen Werte Schlüsse zulassen, ob sie tatsächlich die echte „Eigenleitfähigkeit“ der fraglichen, absolut reinen Verbindung darstellen. Die bei der Reinigung auftretenden Leitfähigkeitseffekte sind im allgemeinen sehr ausgeprägt, sodass die durch methodische Schwierigkeiten bedingten Messfehler praktisch bedeutungslos sind. Diese Überlegungen lassen jedoch zugleich erkennen, dass die umfassendsten tabellarischen Zusammenstellungen der Leitfähigkeit von Nichtelektrolyten gegenstandslos sind, wenn nicht entweder die Originalarbeit zitiert wird oder aber konkrete Angaben über Provenienz und Reinigung der Probe, sowie die gewählte Messtechnik gemacht werden<sup>14</sup>.

Sehr störend macht sich auch bei der Zusammenstellung von Tabellenwerken das unkritische „Abschreiben“ aus bereits vorliegenden Werken bemerkbar. Häufig kann ein fehlerhaftes Resultat in verschiedenen Neuausgaben immer wieder angetroffen werden. (Vergl. z.B. die spezifische Leitfähigkeit von Benzol, welche sowohl im *Taschenbuch für Chemiker und Physiker* von J. D'ANS UND E. LAX<sup>32</sup> als auch im *Handbuch des Chemikers* von B. P. NIKOLSKI<sup>31</sup> mit dem viel zu niedrigen Wert  $< 10^{-18}$  Ohm<sup>-1</sup>cm<sup>-1</sup> angegeben wird; für derartige Fälle lassen sich Dutzende von Beispielen anführen!). CRUSE hat in jüngster Zeit versucht, kritisch gesichtete Tabellenwerte zusammenzustellen<sup>14</sup>, ohne dass damit allerdings in allen Fällen fehlerhafte Messwerte vermieden werden konnten. So wird hier z.B. die Eigenleitfähigkeit von Hexan nach „extremer Reinigung“ mit  $10^{-19}$  Ohm<sup>-1</sup>cm<sup>-1</sup> angegeben<sup>15</sup> — ein Wert, der schon deshalb gar nicht in Betracht kommen kann, weil er im Jahre der Veröffentlichung (1931) weit ausserhalb der damals gegebenen methodischen Möglichkeiten gelegen hat.

Mit derartigen Betrachtungen wird aber zugleich auch die Frage nach dem Sinn von Leitfähigkeitsmessungen als Reinheitskriterium überhaupt angeschnitten. Diese Frage kann positiv in dem Sinne beantwortet werden, dass zunächst einmal alle Arbeiten, welche zur echten Eigenleitfähigkeit eines Nichtelektrolyten führen, strukturelle Rückschlüsse zulassen. Des weiteren gibt es viele Fälle, wo Leitfähigkeitsmessungen zur Untersuchung einer Donator-Akzeptor-Beziehung herangezogen werden können, wozu dann natürlich wiederum hochreine Lösungsmittel — gekennzeichnet durch ihre Eigenleitfähigkeit — erforderlich sind<sup>16</sup>. Schliesslich lassen Leitfähigkeitsmessungen eine Beurteilung der Leistungsfähigkeit von verschiedenen Reinigungsmethoden zu, wobei als Regel gilt, dass der kleinste Leitfähigkeitswert auch vom besten Verfahren erreicht wird.

An Hand einiger willkürlich ausgewählter Beispiele soll gezeigt werden, welche Fortschritte in den Reinigungsmethoden gemacht und was für Korrekturen der bisherigen Werte für die Eigenleitfähigkeit einiger flüssiger Nichtelektrolyte angebracht wurden.

### Wasser

Dieses Lösungsmittel hat besonders im Zusammenhang mit den frühen Elektrolytforschungen eine sehr gründliche Untersuchung der Reinigungsmethoden erfahren. Die damals ganz allgemein üblichen Destillationsmethoden lieferten ein Wasser von einer spezifischen Leitfähigkeit von etwa  $5-7 \cdot 10^{-8}$  Ohm<sup>-1</sup>cm<sup>-1</sup>, während sich aus der Dissoziationskonstanten des Wassers für 18° ein Wert von  $3,82 \cdot 10^{-8}$  Ohm<sup>-1</sup>cm<sup>-1</sup> berechnet. Im Gegensatz zu den recht aufwendigen Mehrfachdestillationen kann heute durch die Anwendung von Ionenaustauschermischbetten ein Wasser von der theoretischen Leitfähigkeit hergestellt werden<sup>17</sup>, wie auch neueste, im National Bureau of Standards in Washington, U.S.A. durchgeführte Untersuchungen gezeigt haben<sup>18</sup>.

### Fluorwasserstoff

Wasserfreier Fluorwasserstoff fand speziell durch die Arbeiten von JANDER als wasserähnliches Lösungsmittel eine gründliche Untersuchung. Dabei lieferte die destillative Reinigung in Edelmetallapparaturen ein Produkt von der Leitfähigkeit  $1,4 \cdot 10^{-5}$  Ohm<sup>-1</sup>cm<sup>-1</sup> bei  $-15^{\circ}$ , während sich aus dem Ionenprodukt der wesentlich niedrigere Wert von  $7,0 \cdot 10^{-6}$  Ohm<sup>-1</sup>cm<sup>-1</sup> für  $20^{\circ}$  berechnet<sup>20</sup>. Erst unter Verwendung

von Apparaturen aus Kel-F (einem hochpolymeren Fluorcarbonderivat) für sämtliche Arbeitsgänge konnte das Einschleppen von Fluoridspuren so weitgehend ausgeschlossen werden, dass hochreiner Fluorwasserstoff mit einer Eigenleitfähigkeit erhalten wurde, der in seiner Leitfähigkeit dem berechneten Wert (unter Berücksichtigung der Temperaturabhängigkeit) sehr nahe kommt. Der Gang der Leitfähigkeit von verschiedenen Destillatfraktionen zeigt die übliche Anreicherung von Verunreinigungen im Vor- und Nachlauf durch Leitfähigkeitserhöhung an<sup>21</sup>.

TABELLE II

LEITFÄHIGKEITSWERTE VERSCHIEDENER FRAKTIONEN BEI DER DESTILLATION VON FLUORWASSERSTOFF

Fraktion Nr.	( $10^6 \kappa (\text{Ohm}^{-1} \text{cm}^{-1})$ bei $0^\circ$ )
1	41.9
2	5.10
3	3.07
4	2.68
5	2.68
6	2.86
7	4.32

Diese Technik der Kontrolle einer Destillation unter ständiger Leitfähigkeitsmessung wird auch bei DK-Messungen häufig angewandt. Sie wurde von EBERT als „verschärfte Siedeanalyse“ bezeichnet<sup>22,23,10</sup>. Im Zusammenhang mit der Bestimmung von Eigenleitfähigkeiten hat sie bereits WALDEN als Reinheitskriterium herangezogen<sup>24</sup> (vergl. Fig. 9).

### Methanol

Methanol enthält herstellungsgemäss durch die hydrierenden Umsetzungen von Kohlenmonoxyd und Wasserstoff infolge einer Sekundärreaktion des Reststickstoffs mit Wasserstoff geringe Mengen niederer aliphatischer Amine, welche bewirken, dass die Leitfähigkeit von technischem Methanol bis über  $10^{-5} \text{ Ohm}^{-1} \text{ cm}^{-1}$  ansteigen kann. Eine Entfernung dieser Amine gelingt leicht durch eine geeignete Behandlung mit Ionenaustauschern<sup>25</sup>.

Schwieriger ist dagegen die Entfernung kleiner, durch Autoxydation gebildeter Mengen von Formaldehyd, welche zu Ameisensäure weiteroxydieren können. Am ehesten gelingt die Entfernung noch bei einer reduktiven Trocknung des Methanols. Wir erprobten dabei Alkalimetall-Amalgame, Aluminium-Amalgam und Calciumhydrid unter Verwendung einer in Fig. 8 gezeigten Umlauftrocknungs-Apparatur<sup>26</sup>.

Calciumhydrid schied bei kritischen Vergleichen durch eine Ammoniakentwicklung infolge eines Nitridgehaltes aus. Am einfachsten war Aluminiumamalgam handzuhaben.

Bei diesen und späteren Untersuchungen haben wir als Reinheitskriterium allerdings nicht die spezifische Leitfähigkeit, sondern den dielektrischen Verlustfaktor  $\tan \delta$  gemessen. Im Gebiet der sogenannten Leitfähigkeitsverluste können beide Grössen jedoch leicht ineinander umgerechnet werden<sup>12</sup>, wenn die bei der  $\tan \delta$ -Messung verwendete Kreisfrequenz  $\omega = 2\pi f$  und die DK der Probe bekannt ist. Es gilt

$$\kappa = \frac{\tan \delta \epsilon \omega}{1.13 \cdot 10^{-13}} \quad (8)$$

Der niedrigste von uns erreichte  $\tan \delta$  des Methanols betrug  $\tan \delta = 82 \cdot 10^{-4}$  für eine Messfrequenz von  $7 \cdot 10^6$  Hz, d.h. für ein  $\omega = 4.39 \cdot 10^7 \text{sec}^{-1}$ . Mit einer DK  $\epsilon = 33.6$  des Methanols errechnet sich hieraus die spezifische Leitfähigkeit zu  $\kappa = 1.07 \cdot 10^{-6} \text{Ohm}^{-1} \text{cm}^{-1}$  bei  $20^\circ$ . Im Schrifttum finden sich allerdings auch noch Angaben über einen niedrigeren Wert von  $\kappa = 5.8 \cdot 10^{-7} \text{Ohm}^{-1} \text{cm}^{-1}$  (wobei der Wert in<sup>31</sup> offenbar

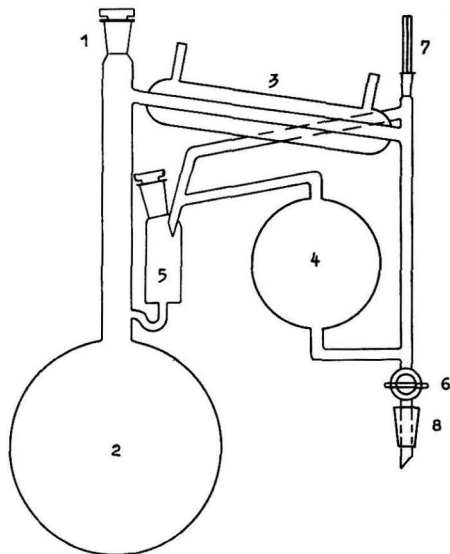


Fig. 8. Umlaufapparatur zur destillativen Trocknung von Lösungsmitteln; 1, Schliff zur Beschickung; 2, Siedekolben; 3, Kühler; 4, Vorratsraum des getrockneten Lösungsmittels; 5, Trockenkammer (Einsetzen von Drahtkörben mit Trockenmittel); 6, Abfüllhahn für 4; 7, Entlüftungskapillare; 8, Schliff zur Messzelle.

aus<sup>32</sup> übernommen wurde). Andererseits wird in denselben Tabellenwerken für  $20^\circ$  auch ein Wert von  $5.8 \cdot 10^{-6} \text{Ohm}^{-1} \text{cm}^{-1}$  genannt. Da eine jede Angabe über Provenienz oder Reinigungs bzw. Messtechnik fehlt, können diese Werte ebenso wenig als verlässlich betrachtet werden, wie der extrem niedrige Wert  $\kappa = 2 \cdot 10^{-9} \text{Ohm}^{-1} \text{cm}^{-1}$  von EVERS UND KNOX<sup>33</sup>.

Bemerkenswert ist in diesem Zusammenhang, dass neuerdings von Herstellern von Feinchemikalien (Fa. Merck AG, Darmstadt) in der Präparatenreihe EL ein hochreines Methanol EL angeboten wird, dessen Leitfähigkeit  $\kappa = 1.2 \cdot 10^{-6} \text{Ohm}^{-1} \text{cm}^{-1}$  angegeben wird, ohne dass allerdings Einzelheiten über die Reinigungsbedingungen bekannt wären.

### Aceton

Im Gegensatz zu Methanol war Aceton weit häufiger Gegenstand von Leitfähigkeitsmessungen. JANDER und Mitarbeiter<sup>34</sup> betonten allerdings, dass Methanol weitaus

\* Eine Bestimmung des Wassergehaltes wurde nicht vorgenommen, da die kapazitive Messstrecke in unserem Fall in die Vorratskugel der in Fig. 8 gezeigten Trockenapparatur eingebaut war und das Präparat somit nicht mit (feuchter) Luft in Berührung gebracht wurde.



schwerer zu entwässern sei. Das mag für die klassischen Trocknungsmittel zutreffen, gilt aber nicht mehr für adsorptive Methoden der Wasserentfernung. So beschreibt WOHLLEBEN<sup>35</sup> die Trocknung von Aceton durch Filtration über aktives Aluminiumoxyd. Die Qualität des Oxydes scheint dabei jedoch eine bestimmende Rolle zu spielen, da nach Arbeiten von EBERT UND LANGHAMMER<sup>36</sup> die ersten Anteile des Filtrates erhebliche Mengen von gebildetem Diacetonalkohols enthalten. Ohne Vorbehalt können dagegen die Linde-Molekularsiebe Typ 4 A und 5 A zur Trocknung von Aceton eingesetzt werden, wie unsere diesbezüglichen Arbeiten zeigten<sup>37,38,39</sup>. Ein Vergleich verschiedener Trocknungsmittel ist in diesem Zusammenhang ebenfalls von Interesse<sup>40</sup>, wenn gleich wir diese Untersuchungen mit Hilfe dielektrischer Messungen als Reinheitskriterium vornahmen. Die DK ist dabei erfahrungsgemäss leichter konstant zu halten und als echter „Eigenwert“ zu betrachten, als die Leitfähigkeit (wenn nicht gerade extreme messtechnische Forderungen gestellt werden, wie das bei der Schaffung von Standardflüssigkeiten zutrifft<sup>10,41</sup>).

Die nachstehende Übersicht lässt durch die Gegenwart nicht unerheblicher Wassermengen im Aceton die bisherigen Trocknungsschwierigkeiten erkennen, die noch dadurch betont werden, dass die übliche Karl-Fischer-Methode zur Wasserbestimmung in Ketonen nicht herangezogen werden kann. CHARLETT<sup>42</sup> gibt deshalb für Betriebskontrollen zur Wasserbestimmung eine hydrolytische Methode an, bei welcher Acetylchlorid durch anwesendes Wasser verseift und als Chlorwasserstoff bestimmt wird. Auch die neue Wasserbestimmungsmethode von JAHR UND FUCHS<sup>43</sup> kann modifiziert zur Bestimmung kleiner Wassermengen in Aceton herangezogen werden.

In den verschiedenen Handbüchern<sup>31,32</sup> wird wiederum übereinstimmend für 20°  $\kappa$  zu  $1.2 \cdot 10^{-7} \text{ Ohm}^{-1} \text{ cm}^{-1}$  angegeben. Damit liegt aber  $\kappa$  zwischen  $5 \cdot 10^{-10}$  und  $1.2 \cdot 10^{-7} \text{ Ohm}^{-1} \text{ cm}^{-1}$ , d.h. um knappe 3 Zehnerpotenzen auseinander! Wie kritiklos dabei Zahlenwerte in die üblichen Laborhandbücher übernommen werden, lässt auch gut ein Vergleich der Temperaturabhängigkeit von  $\kappa$  erkennen.

TABELLE III

VERGLEICH VERSCHIEDENER LEITFÄHIGKEITSWERTE VON ACETON BEI 25°<sup>34</sup>

Autor	$\kappa \cdot 10^8 (\text{Ohm}^{-1} \text{ cm}^{-1})$	Wassergehalt
44	0.051–0.17	0.34 Gew. %
45	2	0.34 Gew. %
46	2.09–2.36	0.18 Gew. %

TABELLE IV

TEMPERATURABHÄNGIGKEIT DER SPEZIFISCHEN LEITFÄHIGKEIT VON ACETON<sup>32</sup>

t°	$\kappa \cdot 10^8 (\text{Ohm}^{-1} \text{ cm}^{-1})$
–15	0.11
0	6
18	2
20	12
25	6

Mit derartigen Werten ist beim besten Willen nichts anzufangen! Hier bleibt nur noch die Möglichkeit offen, die Originalarbeiten einzusehen, die aber gerade in den einschlägigen Handbüchern nicht genannt werden. In wie weit überhaupt gegebenenfalls die im Original zu findenden methodischen Angaben eine Abschätzung der Messrichtigkeit gestatten, ist von Fall zu Fall zu entscheiden. Häufig wird allerdings als einziger Ausweg die Notwendigkeit verbleiben, mit modernen Reinigungsmethoden unter Zuhilfenahme anderer Reinheitskontrollen die fraglichen Messungen selbst nochmals auszuführen.

### Essigsäureanhydrid

Hier liegt ein Lösungsmittel vor, welches in jüngerer Zeit auf Grund seiner ionisierenden Wirkung gegenüber Elektrolyten mehrfach auf seine Eigenleitfähigkeit untersucht wurde. JANDER UND SURAWSKI<sup>6</sup> bringen über die erhaltenen Messwerte

TABELLE V

VERGLEICH DES SIEDEPUNKTES UND DER DK VON ESSIGSÄURE UND IHREM ANHYDRID<sup>23</sup>

Substanz	Kp (760 mm)	DK $\epsilon$ (20°)
Essigsäure	118.1°	6.13
Essigsäureanhydrid	139.4°	22.2

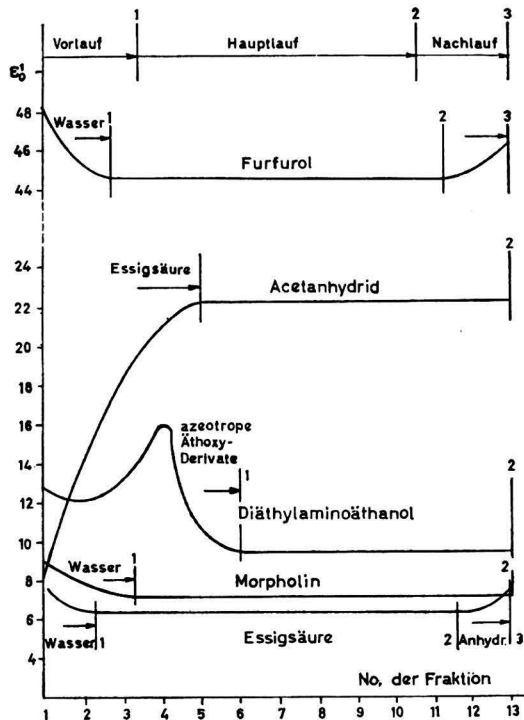


Fig. 9. DK-Volumen-Diagramm verschärfter Siedeanalysen unter Angabe der Hauptverunreinigungen.

einen kritischen Vergleich. Als Hauptverunreinigung enthält Essigsäureanhydrid Essigsäure, welche auf Grund ihres niedrigeren Siedepunktes ohne Schwierigkeiten mit einer guten Kolonne destillativ abgetrennt werden kann. Dabei benutzten wir speziell die DK als Reinheitskriterium, da Anhydrid und Säure recht erhebliche DK-Unterschiede aufweisen.

Wenn die Destillation nach der Methode der „verschärften Siedeanalyse“ durchgeführt wird, lässt sich mit einer geeigneten Durchfluss-Messzelle direkt der Destillatstrom messen und somit feststellen, wenn reines Anhydrid übergeht. Die Kontrolle kann unter Aufnahme eines DK-Volumen-Diagrammes nach Fig. 9 auch graphisch erfolgen.

Rein destillativ reinigten auch GUTMANN UND NEDBALEK<sup>47</sup>, sowie JANDER UND SURAWSKI<sup>6</sup> das Anhydrid. Letztere setzen dem Ausgangsmaterial (Fa. Merck, p.a.-Ware, frei von höheren Homologen) allerdings noch Magnesium- oder Aluminiumspäne zu, die mit vorhandener Essigsäure unter Acetatbildung reagieren. Ähnlich wirkt sich auch ein Zusatz von Natrium aus<sup>48,49</sup>.

Als wahrscheinlichster Wert für die spezifische Leitfähigkeit von Essigsäureanhydrid geben JANDER UND SURAWSKI  $\kappa = 2,3 \cdot 10^{-8} \text{ Ohm}^{-1} \text{ cm}^{-1}$  an, der an einem dreifach fraktioniertem Präparat gemessen wurde.

### *Acetonitril*

Nitrile werden technisch im allgemeinen durch eine katalytische Dehydrierung von Ammoniumsalzen der Carbonsäuren gewonnen. Als Verunreinigung treten folglich noch diese Ammoniumsalze und die intermediär gebildeten Säureamide auf, die beide die Eigenleitfähigkeit der Nitrile stark erhöhen.

Die Reinigung von Acetonitril wird von ELLENDT UND CRUSE<sup>50</sup>, sowie von RÖMBERG<sup>51</sup> nach einer von WALDEN<sup>52</sup> angegebenen Methode durch 6-fache Destillation über Phosphorpentoxyd vorgenommen. Da nach den Beobachtungen von RÖMBERG, das Destillat stets noch Spuren von Phosphorpentoxyd enthielt, wurden noch zwei weitere Destillationen — einmal unter Zusatz frisch geglühter Pottasche und ein zweites Mal ohne jeden Zusatz — angeschlossen. Von den zuletzt genannten Autoren erwähnen besonders ELLENDT UND CRUSE, dass beim 5-tägigen Stehen von hochreinen Acetonitril mit einer spezifischen Leitfähigkeit  $\kappa \leq 2 \cdot 10^{-8} \text{ Ohm}^{-1} \text{ cm}^{-1}$  in einer Glasapparatur unter Luftzutritt die Leitfähigkeit um das rund 10-fache ansteigt, was auf eine Aufnahme von Gasen (?) zurückgeführt wird und durch Spülen der Zelle mit reinem Stickstoff vermieden werden kann. RÖMBERG beobachtete in diesem Zusammenhang, dass beim Spülen von Acetonitril mit Stickstoff durch die Gasbeladung der (platinieren?) Platinelektroden die Zellenkonstante  $k$  beeinflusst wird. Die von ihm genannte Leitfähigkeit von Acetonitril liegt mit ihrem Anfangswert in Übereinstimmung mit den Angaben von ELLENDT UND CRUSE bei  $\kappa < 2 \cdot 10^{-8} \text{ Ohm}^{-1} \text{ cm}^{-1}$ . Nach unseren Erfahrungen dürfte der beobachtete Leitfähigkeitsanstieg jedoch durch eine minimale Feuchtigkeitsaufnahme aus der stets auf Glaswänden vorhandenen und nur bei Rotglut zu entfernenden adsorbierten Wasserschicht oder auch aus dem Stickstoff stammen.

### *Dimethylformamid*

Auf die Schwierigkeiten, welche bei der Reinigung von Dimethylformamid auf-

treten, weisen THOMAS UND ROCHOW<sup>53</sup> hin. Speziell Protonen-Donatoren beeinflussen die Leitfähigkeit von Dimethylformamid stark. Da nun aber gerade bei der Destillation bei Normaldruck bereits eine teilweise Zersetzung der Verbindung in Kohlenmonoxyd und Dimethylamin auftritt und letztere Verbindung ein Protonen-Donator ist, leuchtet ein, dass eine übliche Destillation nur ein Produkt von begrenzter Reinheit liefern kann. Durch saure oder basische Verbindungen wird diese Zersetzung katalysiert.

Nach unseren Beobachtungen<sup>54</sup> ist Dimethylformamid gegen Ultraviolett empfindlich. Als Zersetzungsprodukte treten dabei interessanterweise Dimethylamin und Formaldehyd auf, welche miteinander unter Bildung von Dimethylaminomethanol reagieren.

THOMAS UND ROCHOW<sup>53</sup> vergleichen vier verschiedene Reinigungsmethoden miteinander:

Als Vorreinigung zu allen weiteren Methoden wurde zunächst technisches Dimethylformamid (Difo) mit etwa 10 Vol. % trockenem Benzol versetzt und durch eine Destillation bei Normaldruck mit dem Benzol zugleich das Wasser abdestilliert, sodass ein „Benzol-trockenes“ Präparat anfiel.

*Methode I.* Zu 1 Liter „Benzol-trockenem Difo“ werden 25 g bei 300–400° getrocknetes Magnesiumsulfat gegeben. Die Mischung kommt 24 Stunden auf eine Schüttelmaschine und wird dann nochmals mit der gleichen Menge Magnesiumsulfat versetzt. Anschliessend wird bei einem Druck von 15–20 mm über eine 1 m Kolonne, die mit Stahlwendeln gefüllt ist, destilliert und die Mittelfraktion aufgefangen.

*Methode II.* Benzol-trockenes Difo wird wiederholt mit gepulvertem Bariumoxyd geschüttelt, dekantiert und wie oben destilliert.

*Methode III.* Nach *Methode I* bereits gereinigtes Difo wird mit aktivem Aluminiumoxyd geschüttelt, wobei zu 1 Liter Difo 50 g Oxyd gegeben werden. Anschliessend erfolgt erneuter Aluminiumoxyd-Zusatz und Destillation der Mischung bei einem Druck von 5–10 mm. Die Mittelfraktion wird aufgefangen.

*Methode IV.* Nach *Methode I* gereinigtes Difo wird pro Liter mit 15–20 g Triphenylchlorsilan versetzt und 24 Stunden auf 120–140° erhitzt und anschliessend bei 5 mm destilliert.

Nach diesen 4 Methoden gereinigtes Difo wies folgende Leitfähigkeiten auf:

TABELLE VI

SPEZIFISCHE LEITFÄHIGKEIT VERSCHIEDENER PRÄPARATE VON DIMETHYLFORMAMID<sup>53</sup> (25°)

Reinigungsmethode	spez. Leitfähigkeit $10^7 \times (\text{Ohm}^{-1}\text{cm}^{-1})$
I	0.9–1.5
II	0.4–1.0
III	0.3–0.9
IV	0.6–1.35

Der kleinste Wert der spezifischen Leitfähigkeit liegt bei  $3 \cdot 10^{-8} \text{ Ohm}^{-1}\text{cm}^{-1}$  und ist in der Grössenordnung vergleichbar mit den Werten anderer Bearbeiter, die  $6 \cdot 10^{-8} \text{ Ohm}^{-1}\text{cm}^{-1}$  angeben<sup>55,56</sup>. Auch bei anderen Säureamiden wurden Leitfähigkeitsmessungen zur Reinheitskontrolle herangezogen, wenngleich bei diesen Arbeiten speziell die DK interessierte<sup>57</sup>.

*Dimethylsulfoxyd*

Im Zusammenhang mit einer allgemeinen Untersuchung der Eigenschaften von Dimethylsulfoxyd als Lösungsmittel für anorganische Verbindungen studierten SCHLÄFER UND SCHAFFERNICHT<sup>64</sup> auch die physikalischen Eigenschaften dieses neuen Lösungsmittels.

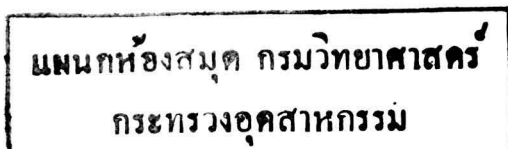
Die Autoren gingen von technischen Dimethylsulfoxyd (Fa. Union Rheinische Braunkohlen Kraftstoff AG, Wesseling) aus, welches neben 0.4% Wasser geringe Mengen von Dimethylsulfid und Spuren von Dimethylsulfon enthielt. Die Reinigung erfolgte durch sehr sorgfältige Destillation in einer Stickstoff-gefüllten Spezialapparatur unter ständiger Leitfähigkeitskontrolle, sowie einer diskontinuierlichen Wasserbestimmung mit Karl-Fischer-Lösung. Der Wassergehalt des hochreinen Produktes lag dabei ausserhalb der Nachweisbarkeitsgrenze und war kleiner als 4 p.p.m. Die Leitfähigkeitsmessungen wurden unter Ausschluss von Luftfeuchtigkeit, in einer Inertgasatmosphäre in einer temperierbaren Glasmesszelle unter Verwendung einer Wechselstrom-Messbrücke vorgenommen.

Für 20° ergab sich eine spezifische Leitfähigkeit  $\kappa = 3 \cdot 10^{-8} \text{ Ohm}^{-1} \text{ cm}^{-1}$  in guter Übereinstimmung mit den Arbeiten von SEARS, LESTER UND DAWSON<sup>65</sup>.

*Kohlenwasserstoffe*

Die bisher betrachteten Verbindungstypen liessen eine Eigendissoziation nach den in Abschnitt 1 angestellten Überlegungen möglich erscheinen. Ausserdem lag die DK in den meisten Fällen so hoch, dass ionogene Verunreinigungen noch in einem gewissen Umfang dissoziieren konnten. Beide Möglichkeiten entfallen bei den aliphatischen Kohlenwasserstoffen. Hier — wie auch bei den Aromaten — liegt die DK zwischen 2 und 3, d.h. so niedrig, dass auf evtl. vorhandene ionogene Verunreinigungen (soweit sich diese überhaupt lösen!) keine dissoziierende Wirkung ausgeübt wird. Eine Eigenleitfähigkeit wäre allenfalls bei den Aromaten unter Beteiligung der  $\pi$ -Elektronen zu erwarten, ein Effekt, der allerdings erst bei höheren kondensierten Systemen zu beobachten ist. Mit Elektronen-Akzeptoren können leitfähigkeitserhöhende Wechselwirkungen auftreten, ohne dass nach den Untersuchungen von Strohmeier<sup>16</sup> in der Leitfähigkeit derartige Einflüsse zu erkennen wären. Im Dipolmoment, bzw. anderen dielektrischen Grössen treten sie dagegen ausgeprägt auf<sup>58,59,60,61</sup>. Von allen bisher untersuchten Substanzen weisen Kohlenwasserstoffe zu erwartender Weise die kleinste Leitfähigkeit auf. Damit werden jedoch auch die methodischen Schwierigkeiten hier am grössten sein, denn der Eigenwiderstand der Messzelle (vergl. Gl. (3)) wird so gut wie immer in der gleichen Grössenordnung wie der Widerstand der mit der Probe gefüllten Messzelle liegen. Der Eigenwiderstand der Messzelle wird bei Verwendung hochwertiger Isolatoren (meist eine Kombination von Isolierkeramik und Teflon) zum guten Teil durch eine Oberflächenleitfähigkeit zwischen den beiden Elektroden der Messzelle über die stützende und trennende Isolation hinweg aufgelöst. Durch die Verwendung von Schutzring-Messzellen nach Fig. 10 kann dieser Kriechstromweg vermieden werden, ohne dass allerdings die meisten handelsüblichen Tero-Ohm-Meter den Anschluss solcher Messzellen zulassen<sup>9,62</sup>.

Eine weitere Fehlermöglichkeit ergibt sich dadurch, dass der Widerstand der mit der Probe gefüllten Messzelle bereits mit dem Eingangswiderstand des Anzeigeverstärkers (Wechselspannungsverstärker oder Röhrenvoltmeter) vergleichbar wird. Auch mangelhafte Abschirmung der Messzelle (Glasmesszelle!) führt zu beträchtlichen Messfehlern.



Bereits bei der kritischen Besprechung der bisher betrachteten Substanzen mussten erhebliche Unsicherheiten in der Bewertung der Messergebnisse verschiedener Autoren festgestellt werden. Das trifft hier noch viel ausgeprägter zu. So wurde bereits im Abschnitt 3 auf die mit  $\kappa \cdot 10^{-19} \text{ Ohm}^{-1} \text{ cm}^{-1}$  angegebenen und infolge der fehlenden

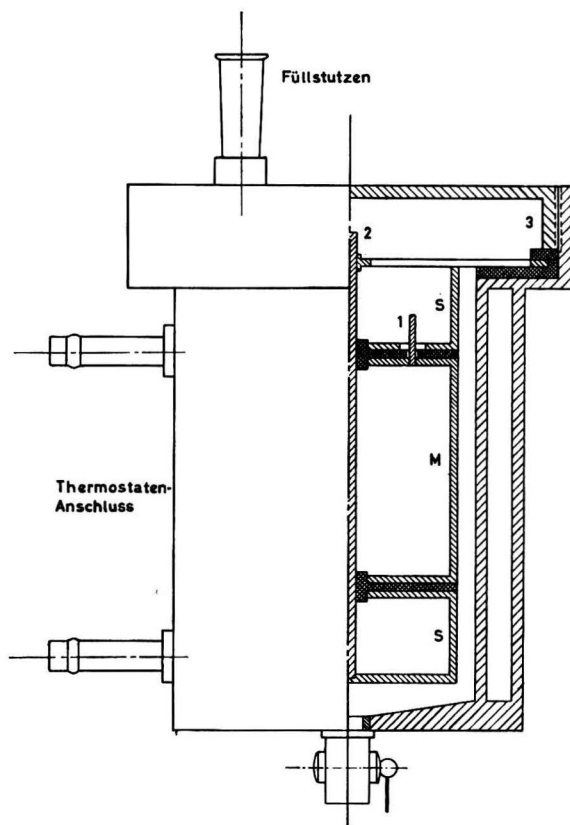


Fig. 10. Schematisierter Aufbau einer Schutzring-Messzelle für Flüssigkeiten (Fa. W.T.W., Weilheim/Obb.). M, geschützte Elektrode; S, oberer und unterer Schutzring.

experimentellen Voraussetzungen gewiss stark fehlerhaften Leitfähigkeit hingewiesen. Die Regel, dass von allen gewählten Reinigungsmethoden jene, welche die kleinste Leitfähigkeit liefert, auch die beste ist, gilt hier nicht mehr<sup>15</sup>. Eine ähnliche Einschränkung ergibt sich für die Untersuchungen von STROHMEIER<sup>6</sup>, welcher zwar die Reinigung sehr sorgfältig betrieb, alle Messungen jedoch in einer Glasapparatur vornahm und für *n*-Heptan bei 20°,  $\kappa = 6.6 \cdot 10^{-14} \text{ Ohm}^{-1} \text{ cm}^{-1}$ , für Benzol  $\kappa = 3.8 \cdot 10^{-14} \text{ Ohm}^{-1} \text{ cm}^{-1}$  fand.

Es kann über die Leitfähigkeit von Kohlenwasserstoffen damit gegenwärtig nur soviel gesagt werden, dass ihre spezifische Leitfähigkeit wohl kleiner als  $10^{-14} \text{ Ohm}^{-1} \text{ cm}^{-1}$  sein wird. Die Reinigungsmethoden spielen dabei eine verhältnismässig untergeordnete Rolle, sofern die Proben bestmöglich getrocknet werden. Indirekte Aussagen

über die Leitfähigkeit von Kohlenwasserstoffen macht GUIZONNIER<sup>63</sup>, welcher speziell den Elektrodeneinfluss und den Zeitfaktor im Zusammenhang mit den nach Anlegen bestimmter Messspannungen fließenden Strömen untersucht. Auch aus diesen Messungen gehen die methodischen Schwierigkeiten überzeugend hervor.

#### 4. SCHLUSSBETRACHTUNGEN

In den vorangegangenen Abschnitten wurden die Schwierigkeiten, welche bei der Reinigung und der Leitfähigkeitsmessung von flüssigen Nichtelektrolyten auftreten, näher beschrieben. Zugleich ist an Hand willkürlich ausgewählter Einzelbeispiele die sehr unterschiedliche Verlässlichkeit und Messrichtigkeit der von verschiedenen Bearbeitern angegebenen Werte diskutiert worden. Nachstehend soll noch einmal kurz zusammengefasst werden, welche Forderungen bei der Messtechnik selbst zu erfüllen sind:

##### 4.1 Messgeräte

*Messungen mit Gleichspannung.* Die Messspannung  $U_M$  soll mindestens 100 V betragen und ausserdem zu variieren sein (etwa von 100–1000 V). Der Eingangswiderstand des Anzeigeverstärkers soll so gross wie möglich sein. Durch die Verwendung von Spezial-Elektrometerröhren sind z.B. bei der Spannungsteilerschaltung Eingangswiderstände bis zu  $10^{14}$  Ohm zu erreichen. Modulierte Gleichstromverstärker liegen im Eingangswiderstand etwa um eine Zehnerpotenz niedriger und sind weniger geeignet.

Da der Messwert einen zu den Schwankungen der Messspannung  $U_M$  direkt proportionalen Fehler enthält, ist durch Stabilisierungsmittel für grösstmögliche Konstanz von  $U_M$  zu sorgen.

*Messungen mit Wechselstrom.* Die Messspannung  $U_M$  braucht im Gegensatz zu den Gleichspannungs-Messungen nur wenige Volt zu betragen. Dagegen ist die Messfrequenz  $f$  möglichst niedrig zu wählen, um Fehlereinflüsse von als Shuntkreis auftretenden Blindwiderständen auszuschalten (vergl. Gl. (4) und (5)). Bei direkt anzeigenden Geräten (Ausschlagsmethode) muss der Anzeigeverstärker phasenempfindlich sein. Beide Gerätegruppen sollen zweckmässigerweise für den Anschluss von Schutzringmesszellen eingerichtet sein.

##### 4.2 Messzellen

Aus Gründen der elektrischen Abschirmung (Streifeld) und der besseren Möglichkeit zur Temperierung ist Metallzellen der Vorzug zu geben. Die Isolation soll mit oberflächenglasierter Isolierkeramik unter Einbezug von Dichtungsringen aus Teflon erfolgen. Die an sich denkbare reine Teflonisolation scheidet an der — besonders bei höheren Temperaturen störenden — Plastizität des Materials. Es ist von Vorteil, wenn die Zelle zur Reinigung zerlegt werden kann.

Für den Bau des Zellenkörpers genügt V4A-Stahl hohen Korrosionsansprüchen. Häufig wird auch mit vernickeltem oder verchromtem Messing auszukommen sein. Die Elektrodenoberflächen werden nicht platinieren.

Schutzring-Messzellen ist gegenüber ungeschützten Bauformen stets der Vorzug zu geben.

Der Eigenwiderstand  $R_z$  der Messzelle wird empfindlich durch Verunreinigung der

Isolierelemente beeinflusst. Er ist des öfteren zu kontrollieren.  $R_Z$  wird häufig durch Wasserfilme verfälscht. Nach jeder Messreihe wird die Messzelle deshalb nach sorgfältiger Reinigung bei etwa 200° (Hartlötung!) getrocknet und in einem Exsiccator aufbewahrt.

Zur Berechnung der auf die Probe wirkenden Feldstärke  $\xi$  ist bei den Messwerten zweckmäßigerweise der Elektrodenabstand  $d$  und die Messspannung  $U_M$  anzugeben.

### 4.3 Reinigung der Probe

Stets ist die Provenienz zu nennen. Sehr angebracht ist es, unter Zuhilfenahme moderner Analysenmethoden (Absorptionsspektrographie im Ultrarot und Ultraviolet, Gas-Chromatographie, kolorimetrische Methoden zur Bestimmung funktioneller Gruppen) vor Beginn der Reinigungsoperationen zu bestimmen, welche Verunreinigungen anwesend sind. Die gewählte Reinigungsmethode ist möglichst genau zu beschreiben. Der Erfolg der Reinigung ist unter Heranziehen von Hilfsmethoden (siehe oben) zu kontrollieren.

Bei der Angabe der spezifischen Leitfähigkeit ist neben einer kurzen aber eindeutigen Beschreibung des Gerätes und der Messzelle Wert auf die Angabe folgender Größen zu legen: Temperatur der Probe, Zellenkonstante  $k$ , Elektrodenabstand  $d$ , Messspannung  $U_M$  (bei Wechselspannungs-Messungen auch Nennung der Messfrequenz).

Nur bei Kenntnis dieser Angaben kann die Richtigkeit der Ergebnisse verschiedener Bearbeiter kritisch beurteilt werden.

### DANK

Soweit es sich um eigene Messungen handelt, wurden diese im Institut zur Entwicklung chem.-phys. Analysenmethoden, Weilheim/Obb. durchgeführt.

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# INVESTIGATION OF THE FORMAL REDOX POTENTIALS OF THE SYSTEM $Pb^{4+}/Pb^{2+}$ WITH REGARD TO THE USE OF LEAD TETRAACETATE IN VOLUMETRIC ANALYSIS

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## INTRODUCTION

During the last few years we have investigated the use of lead tetraacetate as a volumetric agent for the oxidation of inorganic<sup>1-5</sup> and organic<sup>6-9</sup> systems. Lead tetraacetate is a strong oxidizing agent, the redox potential of which has been measured in non-aqueous media by TOMÍČEK AND VALCHA<sup>10</sup>. These authors state that the value of the redox potential in glacial acetic acid, in the presence of alkaline acetate is, at the most, 1.32 V, and in the presence of perchloric acid 1.44 V. For the normal redox potential of the system  $Pb^{4+}/Pb^{2+}$  the values 1.7 V and 1.75 V are given, respectively<sup>11,12</sup>. Since, unlike previous authors, we have found lead tetraacetate suitable for direct as well as indirect titrations in aqueous media, either containing mineral acids or suitably buffered, we give in the present communication its measured formal redox potentials in those media in which, according to our experience, the oxidations are best carried out. For the oxidation of inorganic systems this is a medium of hydrochloric acid, and for organic systems a medium of dilute acetic acid, possibly with addition of potassium acetate.

## EXPERIMENTAL

### *Reagents*

A 0.1 N lead tetraacetate solution in glacial acetic acid free of divalent lead ions was prepared by reaction of the minimum amount of  $Pb_3O_4$  with glacial acetic acid, as already described<sup>2</sup>. Solutions of lower molarity were prepared by accurate dilution. The strength of the solutions was determined by titration with a standard hydrazine sulphate solution<sup>1</sup> or with monovalent thallium<sup>3</sup>. The other solutions used were prepared from substances marked as AR (Lachema, Merck).

### *Apparatus*

The potentials were measured with an electronic pH-Meter Acidimetr EK 21 (Kovodružba, Prague) with a platinum indicating and a saturated calomel reference electrode. All potential values mentioned are calculated for the standard hydrogen electrode.

## RESULTS

We have measured the formal redox potential either from the course of the potentiometric titration curve of a suitable system, taking the potential value at double the reagent consumption needed for equivalence, or by measuring the potential of an equimolar mixture of the oxidised and reduced forms of the system studied. The values given in the figures are averages of multiple measurements.

*The formal redox potential of  $Pb^{4+}/Pb^{2+}$  in hydrochloric acid medium*

Both the above-mentioned methods of measurement were complicated by the rapid hydrolysis of tetravalent lead, which in hydrochloric acid medium does not interfere in the titration, but which rapidly becomes evident at double excess of the reagent against the titrated system.

It has, however, been found possible to measure the formal redox potential from the titration curve, whereas after preparation of the equimolar mixture of  $Pb(IV)$ - and  $Pb(II)$ -acetate hydrolysis started before it was possible to carry out the measurement.

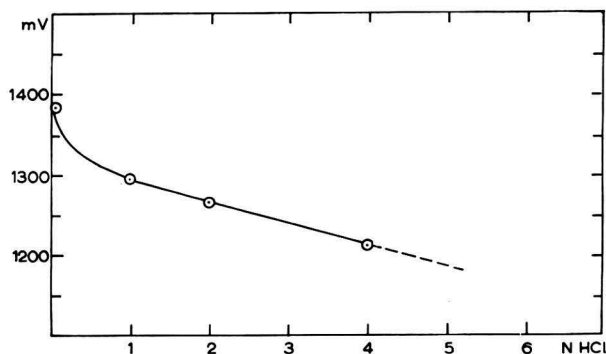


Fig. 1. Dependence of the formal redox potential of the system  $Pb^{4+}/Pb^{2+}$  on HCl concentration.

We have measured the formal redox potential of the system  $Pb^{4+}/Pb^{2+}$  from titration curves of bivalent iron and trivalent arsenic in a medium of 0.03–4 *N* HCl. It was impossible to carry out the measurements in more dilute hydrochloric acid solutions, because practically immediately on reaching the equivalence-point the tetravalent lead hydrolysed. In solutions more concentrated than 4 *N* HCl, chlorine was liberated relatively rapidly from the hydrochloric acid by an excess of the reagent, influencing the potential of the indicating electrode.

In practice we proceeded in such a way that we titrated 3.5 mg  $As^{3+}$  or 11 mg  $Fe^{2+}$  in 50 ml volume in a medium of 0.03–4 *N* HCl against a 0.1 *N* lead tetraacetate solution, free of  $Pb^{2+}$  ions. At the equivalence-point we added the necessary excess of the reagent at once, and immediately on stabilisation of the potential we measured its value. The dependence of the formal redox potential values on hydrochloric acid concentration are given in Fig. 1. It can be seen that the formal redox potential values decrease with increasing hydrochloric acid concentration. In order to verify whether the dependence mentioned is caused only by the acidity of the solution, or is also influenced by the character of the acid, we have carried out the measurement of the formal redox potential value also in a medium of 1.1–5.8 *N*  $HClO_4$ .

*The formal redox potential of Pb<sup>4+</sup>/Pb<sup>2+</sup> in perchloric acid medium*

It has been found possible to measure directly the potential of an equimolar mixture of Pb(IV)- and Pb(II)-acetate in perchloric acid medium. The measured values, which are given in Table I, have been obtained by measuring the e.m.f. of the cell Pt electrode-S.C.E. in 50 ml of a solution containing 1 ml 0.05 M PbAc<sub>2</sub> and 1 ml 0.05 M PbAc<sub>4</sub>. The potential values were always read directly on stabilisation of the potential of the indicating electrode after addition of lead tetraacetate.

It can be seen from Table I, that in contrast to the hydrochloric acid medium, the

TABLE I  
THE FORMAL REDOX POTENTIAL OF THE SYSTEM Pb<sup>4+</sup>/Pb<sup>2+</sup> IN PERCHLORIC ACID MEDIUM

HClO <sub>4</sub> (N)	Formal potential (mV vs. S.H.E.)
1.1	1660
1.1	1650
2.3	1670
3.4	1660
5.8	1700
5.8	1680

formal redox potential value changes only little in solutions acidified by perchloric acid, but in comparison with the hydrochloric acid medium the potentials are more than 300 mV higher, and approach the value of the normal redox potential of the system Pb<sup>4+</sup>/Pb<sup>2+</sup>.

This observation permits us to assume that it will be possible to use perchloric acid as a medium for the oxidation of some systems by lead tetraacetate, which are not satisfactorily oxidised in hydrochloric or sulphuric acid media.

The energetic oxidising effect of lead tetraacetate in perchloric acid medium is also shown by our observation that, in a medium of 1 N perchloric acid, tervalent ruthenium is oxidised to RuO<sub>4</sub>, even though the formal potential of the system Ru<sup>4+</sup>/RuO<sub>4</sub> in this medium is 1.4 V<sup>13</sup>.

*The formal redox potential of Pb<sup>4+</sup>/Pb<sup>2+</sup> in acetic acid medium*

We have first measured the values of the formal redox potential Pb<sup>4+</sup>/Pb<sup>2+</sup> in media of 30–100% acetic acid, the concentration of Pb(IV)-acetate and Pb(II)-acetate being 0.01 M. In solutions of lower acetic acid concentration than 30%, the Pb(IV)-salt hydrolysed rapidly. In solutions of 50–90% acetic acid stabilisation of the potential of the indicating electrode was slow (about 3 min). The results of the measurements are given in Figs. 2 and 3, curves (a). In the same way the dependence of the formal redox potential of the system studied on acetic acid concentration was also studied in the presence of 0.4 M potassium acetate (see Fig. 2, curve (b)). The latter medium has been found to be especially useful for the oxidation of a number of organic substances<sup>9</sup>.

We have further investigated the dependence of the formal redox potential values (in solutions of varying acetic acid concentration) on the concentration of Pb(IV) and Pb(II) ions. In our experiments the concentrations of Pb<sup>2+</sup>, equal to the concentration of Pb<sup>4+</sup>, were 10<sup>-2</sup>, 2·10<sup>-3</sup>, 2.5·10<sup>-4</sup> and 10<sup>-4</sup> M, respectively. With decreasing con-

centration of  $\text{Pb}^{2+}$  and  $\text{Pb}^{4+}$  it was found possible to carry out the measurement also in solutions containing less than 30% acetic acid. In solutions containing 30–90% acetic acid stabilisation of the potential was again slow. Results of the measurements are given in Fig. 3.

The slow stabilisation of the potential and its dependence on the concentration of  $\text{Pb}^{4+}$  and  $\text{Pb}^{2+}$  ions, clearly to be seen in Fig. 3, have led us to the conclusion that in

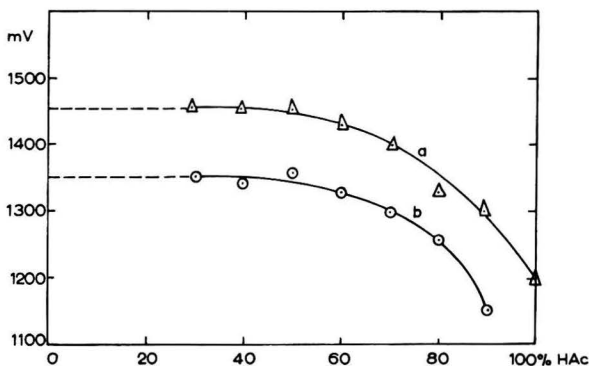


Fig. 2. Dependence of the formal redox potential of the system  $\text{Pb}^{4+}/\text{Pb}^{2+}$  on acetic acid concentration.

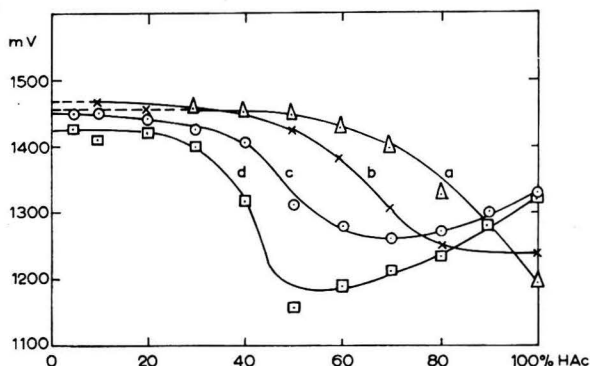


Fig. 3. Dependence of the formal redox potential of the system  $\text{Pb}^{4+}/\text{Pb}^{2+}$  on acetic acid concentration with varying concentrations of the system studied in the solution. The  $\text{Pb}^{4+}$  and  $\text{Pb}^{2+}$  concentrations are: (a)  $10^{-2} M$ ; (b)  $2 \cdot 10^{-3} M$ ; (c)  $2.5 \cdot 10^{-4} M$ ; (d)  $10^{-4} M$ .

diluting the acetic acid various complexes of lead tetraacetate and water are formed. This assumption has already been proposed by CRIGEE AND BÜCHNER<sup>14</sup>, who explain the stronger oxidising effect of lead tetraacetate in water-containing solutions by the formation of the compound  $\text{PbAc}_2(\text{OH})_2$ , which has a stronger oxidising effect than "real"  $\text{PbAc}_4$ . We believe that the dependence of the formal redox potential on the  $\text{Pb}^{4+}$  and  $\text{Pb}^{2+}$  concentration in the solution is caused by the slow formation of complexes of lead tetraacetate with water in very dilute  $\text{Pb}^{4+}$  ion solutions, whereas in the more concentrated solutions equilibrium is reached relatively rapidly.

This assumption is further proved by the following experiment. The formal redox potential of the system was measured in solutions of 5–100% acetic acid containing  $\text{Pb}^{4+}$  and  $\text{Pb}^{2+}$  ions at the concentrations of  $2.5 \cdot 10^{-4} M$  immediately after mixing the solutions (Fig. 4, curve (a)), after standing for 45 min (curve (b)) and after 6 h (curve (c)). It can be seen from Fig. 4, that equilibrium is established in the solution very slowly.

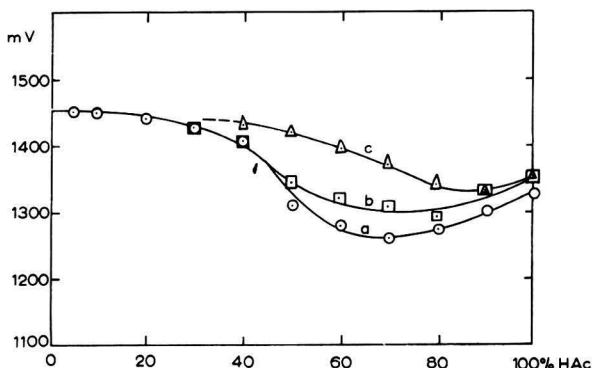


Fig. 4. Dependence of the formal redox potential of the system  $\text{Pb}^{4+}/\text{Pb}^{2+}$  on time:  $\text{Pb}^{4+}$  and  $\text{Pb}^{2+}$  ion concentrations are  $2.5 \cdot 10^{-4} M$ ; measured after (a) 5 min; (b) 45 min; and (c) 6 h.

From the measurements carried out in acetic acid media the following conclusions have been drawn. The value of the formal redox potential of the system studied in solutions containing less than 30% acetic acid is about 1450 mV. In solutions also containing 0.4 M potassium acetate the value of the formal redox potential is always about 100 mV lower, irrespective of the acetic acid concentration. The value of the formal redox potential depends on the concentration of acetic acid and of  $\text{Pb}^{4+}$  and  $\text{Pb}^{2+}$  ions in the solution, and varies with time, this probably being due to the formation of complexes of lead tetraacetate with water.

Even though the problem studied deserves further detailed investigation, the results obtained in the present work are of value also from a practical point of view. For the direct titration of inorganic systems, the observation that the formal redox potential of  $\text{Pb}^{4+}/\text{Pb}^{2+}$  is much higher in perchloric acid than in hydrochloric acid is especially important. The observed dependence of the redox potential values on the concentration of acetic acid and on the concentration of the oxidising agent will facilitate the choice of suitable reaction conditions for the indirect determination of some organic substances, especially when using volumetric solutions of lower molarity.

#### SUMMARY

The values of the formal redox potential of the system  $\text{Pb}^{4+}/\text{Pb}^{2+}$  have been measured in media of hydrochloric acid, perchloric acid and acetic acid (also with the addition of potassium acetate). The dependence of the formal redox potential value on the concentration of the acids mentioned, on the concentrations of the  $\text{Pb}^{4+}$  and  $\text{Pb}^{2+}$  ions in the solution, and on time, has been investigated.

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## THE TRANSFER OF IONS THROUGH THE DIFFUSION LAYER

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## INTRODUCTION

Up to the present time a clear picture of the contribution of the various ions to the passage of current through a diffusion layer being formed near the electrode is lacking except for the fairly uncomplicated cases in which forced convection is applied during electrolysis<sup>1</sup>, and yet this problem is undoubtedly of importance for our understanding of polarography. However, it is not possible to give a perfectly exact derivation relating to a growing mercury drop. In view of this the relation will be examined for a flat electrode, which may be conceived to be the ending of a horizontal tube. Account will be taken neither of convection nor of the fact that the diffusion coefficient may also depend upon the concentration. In this connection it may be observed that in the first calculations of the intensity of the diffusion current the starting-point was also the behaviour at a flat electrode<sup>2</sup>. Indeed, the said restrictions do not prevent the conclusions which may be drawn from the following calculations from also being valuable for the case of the growing mercury drop. In particular this will be the case with the equation, to be derived immediately from the calculations, for the proportion between the limiting currents in the presence and in the absence of supporting electrolyte.

By way of illustration we shall consider the electrolysis of a solution of zinc chloride in the presence of a large excess of lithium chloride as well as in the absence of such an addition. This instance has been chosen deliberately to prevent the possibility of certain lines approximately coinciding during the later construction of Figs. 2 and 3. Moreover, the diffusion coefficients of  $\text{Zn}^{2+}$ ,  $\text{Li}^+$  and  $\text{Cl}^-$  can be represented approximately by round figures, *viz.*  $\frac{1}{4} \cdot 10^{-5}$ ,  $\frac{1}{3} \cdot 10^{-5}$ , and  $\frac{2}{3} \cdot 10^{-5}$   $\text{cm}^2 \text{sec}^{-1}$  respectively, which leads to a simplification of the calculations.

In the following discussion we imagine the process to be carried out in such a way that the concentration of the zinc ion at the electrode is negligible as compared with that in the body of the solution (limiting current).

## LIST OF SYMBOLS USED

<i>A</i>	surface of the cross-section;
<i>B</i>	constant (eqns. 19 and 20);
<i>C</i>	concentration;
<i>D</i>	diffusion constant;
<i>E</i>	potential;



$Fy$	Faraday constant;
$K$	force;
$N$	number of particles;
$R$	gas constant;
$T$	degrees Kelvin;
$V$	proportion between limiting currents;
$h$	hydrodynamical mobility;
$i = 1, 2, 3$	components, respectively $Zn^{2+}$ , $Li^+$ and $Cl^-$ ;
$j$	current density;
$i_j$	total current density;
$m_j$	migration component;
$a_j$	diffusion component;
$n$	valency;
$t$	time;
$u$	velocity;
$x$	distance from electrode surface;
$\bar{\mu}$	electrochemical potential.

## METAL DEPOSITION IN THE PRESENCE OF SUPPORTING ELECTROLYTE

We shall start from the fact that the velocity  $u$  of a particle in a solution is proportional to the force  $K$  exerted upon it<sup>3</sup>, which is expressed in the equation:

$$u_i = K_i h_i \quad (1)$$

The force  $K_i$  is to be regarded as the negative gradient of the electrochemical potential  $\bar{\mu}_i$ , accordingly:

$$K_i = -\frac{\partial \bar{\mu}_i}{\partial x} = -RT \frac{\partial \ln C_i}{\partial x} - n_i Fy \frac{\partial E}{\partial x} \quad (2)$$

The number of particles passing through a given cross-section  $A$ , situated at a distance  $x$ , to the right of the electrode, may be represented by:

$$x \left[ \frac{dN_i}{dt} \right] = A u_i C_i \quad (3)$$

The combination of eqns. 1, 2 and 3 leads to

$$x \left[ \frac{dN_i}{dt} \right] = -AD_i \left( \frac{\partial C_i}{\partial x} + \frac{n_i Fy}{RT} C_i \frac{\partial E}{\partial x} \right) \quad (4)$$

since the diffusion coefficient  $D$  is equal to  $hRT$ . At a distance  $x + \Delta x$  from the electrode, the passage through a surface of equal area is:

$$x + \Delta x \left[ \frac{dN_i}{dt} \right] = -AD_i \left\{ \left( \frac{\partial C_i}{\partial x} + \frac{\partial^2 C_i}{\partial x^2} \Delta x \right) + \frac{n_i Fy}{RT} \left( C_i + \frac{\partial C_i}{\partial x} \Delta x \right) \left( \frac{\partial E}{\partial x} + \frac{\partial^2 E}{\partial x^2} \Delta x \right) \right\} \quad (5)$$

The change of the concentration in the disc of liquid with a thickness  $\Delta x$  can then be calculated as the difference between eqns. 4 and 5, divided by the volume of the disc. This leads to the following differential equation:

$$\frac{\partial C_i}{\partial t} = D_i \frac{\partial^2 C_i}{\partial x^2} + \frac{n_i Fy}{RT} D_i \frac{\partial C_i}{\partial x} \frac{\partial E}{\partial x} + \frac{n_i Fy}{RT} D_i C_i \frac{\partial^2 E}{\partial x^2} \quad (6)$$

The presence of a large excess of supporting electrolyte makes the solution sufficiently conductive, so that because of the small value of  $\partial E/\partial x$  the second term from the right-hand member of eqn. 6 may be neglected (in the absence of an indifferent electrolyte, on the other hand, this term is important).

The third term may only be neglected for the zinc ion, because the concentration of the latter is about one hundredth of that of the lithium and the chloride ion, while the difference between the other quantities is only small.

By these simplifications we finally get the following three differential equations:

$$\frac{\partial C_1}{\partial t} = D_1 \frac{\partial^2 C_1}{\partial x^2} \quad (7)$$

$$\frac{\partial C_2}{\partial t} = D_2 \frac{\partial^2 C_2}{\partial x^2} + \frac{Fy}{RT} D_2 C_2 \frac{\partial^2 E}{\partial x^2} \quad (8)$$

$$\frac{\partial C_3}{\partial t} = D_3 \frac{\partial^2 C_3}{\partial x^2} - \frac{Fy}{RT} D_3 C_3 \frac{\partial^2 E}{\partial x^2} \quad (9)$$

The solution of eqn. 7 is known from the polarographic literature<sup>4</sup>; it is

$$C_1 = *C_1 \frac{2}{\sqrt{\pi}} \int_0^{\frac{x}{\sqrt{4D_1 t}}} e^{-p^2} dp \quad (10)$$

From eqns. 8 and 9 the quantity  $\partial^2 E/\partial x^2$  can be eliminated. This leads to the following equation:

$$D_2 C_2 \frac{\partial C_3}{\partial t} + D_3 C_3 \frac{\partial C_2}{\partial t} = D_2 D_3 C_2 \frac{\partial^2 C_3}{\partial x^2} + D_2 D_3 C_3 \frac{\partial^2 C_2}{\partial x^2} \quad (11)$$

We now introduce the relation for electroneutrality:

$$C_3 = C_2 + 2C_1 \quad (12)$$

In consequence of this, eqn. 11 is transformed into:

$$(D_2 C_2 + D_3 C_2 + 2D_3 C_1) \frac{\partial C_2}{\partial t} + 2D_2 C_2 \frac{\partial C_1}{\partial t} = 2D_2 D_3 (C_1 + C_2) \frac{\partial^2 C_2}{\partial x^2} + 2D_2 D_3 C_2 \frac{\partial^2 C_1}{\partial x^2} \quad (13)$$

Through the use of eqn. 7 and neglecting  $C_1$  as compared with  $C_2$ , eqn. 13 may be reduced to:

$$D_1 (D_2 + D_3) \frac{\partial C_2}{\partial t} = 2D_1 D_2 D_3 \frac{\partial^2 C_2}{\partial x^2} + 2D_2 (D_3 - D_1) \frac{\partial C_1}{\partial t} \quad (14)$$

This still contains the differential quotient  $\partial C_1/\partial t$ , which can be calculated by differentiating eqn. 10 to  $t$ . We then find:

$$\frac{\partial C_1}{\partial t} = -\frac{1}{2}\pi^{-1/2} D_1^{-1/2} *C_1 x t^{-3/2} e^{-x^2/4D_1 t} \quad (15)$$

Introduction of (15) into (14) finally yields the desired differential equation for  $C_2$  as a function of  $x$  and  $t$ :

$$\frac{\partial C_2}{\partial t} = 2 \frac{D_2 D_3}{D_2 + D_3} \frac{\partial^2 C_2}{\partial x^2} - \pi^{-1/2} D_1^{-3/2} D_2 \frac{D_3 - D_1}{D_2 + D_3} * C_1 x t^{-3/2} e^{-x^2/4 D_1 t} \quad (16)$$

The corresponding equation for  $C_3$  has the same form:

$$\frac{\partial C_3}{\partial t} = 2 \frac{D_2 D_3}{D_2 + D_3} \frac{\partial^2 C_3}{\partial x^2} - \pi^{-1/2} D_1^{-3/2} D_3 \frac{D_1 - D_2}{D_2 + D_3} * C_1 x t^{-3/2} e^{-x^2/4 D_1 t} \quad (17)$$

The solution of these differential equations, subject to the initial and boundary conditions holding good for this problem — *viz.*  $x \geq 0, t = 0: C_2 = *C_2$  and  $C_3 = *C_3$ ;  $x = 0, 0 < t < \infty: C_2 = C_3 = {}^\circ C_{2,3}$  (constant) — may be obtained with the aid of Laplace transformations. The result, obtained through the courtesy of the Institute for Applied Mathematics, is as follows:

$$C_{2,3} = {}^\circ C_{2,3} - ({}^\circ C_{2,3} - *C_{2,3} - B_{2,3}) \frac{2}{\sqrt{\pi}} \int_0^{\frac{x}{\sqrt{4Dt}}} e^{-p^2} dp - B_{2,3} \frac{2}{\sqrt{\pi}} \int_0^{\frac{x}{\sqrt{4D_1 t}}} e^{-p^2} dp \quad (18)$$

Into this, the following abbreviations have been introduced:

$$B_2 = 2 \frac{D_2}{D - D_1} \frac{D_3 - D_1}{D_2 + D_3} *C_1 \quad (19)$$

$$B_3 = 2 \frac{D_3}{D - D_1} \frac{D_1 - D_2}{D_2 + D_3} *C_1 \quad (20)$$

$$D = 2 \frac{D_2 D_3}{D_2 + D_3} \quad (21)$$

Now the value of the constant  ${}^\circ C_{2,3}$  still has to be determined. Because  $\text{Li}^+$  as well as  $\text{Cl}^-$  does not react at the electrode, the rate of supply there is equal to zero; in mathematical terms:

$${}^\circ \left[ \frac{dN_2}{dt} \right] = 0 \quad \text{and} \quad {}^\circ \left[ \frac{dN_3}{dt} \right] = 0 \quad (22)$$

By making use of eqn. 4 we get:

$${}^\circ \left[ \frac{\partial C_2}{\partial x} \right] = -{}^\circ C_2 \frac{Fy}{RT} {}^\circ \left[ \frac{\partial E}{\partial x} \right] \quad (23)$$

and

$${}^\circ \left[ \frac{\partial C_3}{\partial x} \right] = {}^\circ C_3 \frac{Fy}{RT} {}^\circ \left[ \frac{\partial E}{\partial x} \right] \quad (24)$$

Because  ${}^\circ C_2 = {}^\circ C_3$ , eqns. 23 and 24 yield the relation:

$${}^\circ \left[ \frac{\partial C_2}{\partial x} \right] = - {}^\circ \left[ \frac{\partial C_3}{\partial x} \right] \quad (25)$$

By differentiation of eqn. 12 we get:

$$2 \left[ \frac{\partial C_1}{\partial x} \right] + \left[ \frac{\partial C_2}{\partial x} \right] = \left[ \frac{\partial C_3}{\partial x} \right] \quad (26)$$

Combination of (25) and (26) gives:

$$\left[ \frac{\partial C_1}{\partial x} \right] = - \left[ \frac{\partial C_2}{\partial x} \right] = \left[ \frac{\partial C_3}{\partial x} \right] \quad (27)$$

By making use of eqn. 27 together with eqns. 10 and 18, we find the concentration of the supporting electrolyte at the electrode:

$${}^{\circ}C_2 = {}^*C_2 + B_2 + ({}^*C_1 - B_2)\sqrt{D/D_1} \quad (28)$$

The full lines of Fig. 1 indicate the course of the concentrations of the three ions in the diffusion layer. The time is fixed at one second (this also applies to Figs. 2 and 3), because the calculations then become much simpler.

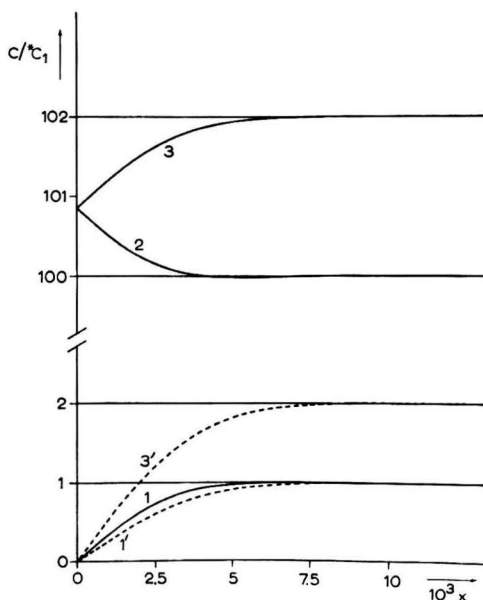


Fig. 1. Relative concentration as function of the distance from the electrode, one second after the beginning of electrolysis: 1,  $Zn^{2+}$ ; 2,  $Li^+$ ; 3,  $Cl^-$  in the presence of supporting electrolyte; 1',  $Zn^{2+}$ ; 3',  $Cl^-$  in the absence of supporting electrolyte.

In the polarographic literature mention is made<sup>5</sup> only once, and then only qualitatively, of this course of the concentrations.

KIMBALL AND GLASSNER<sup>6</sup> gave a solution of a polarographically less interesting example, which they moreover obtained by numerical integration.

It is now possible to consider the passage of the current through the diffusion layer more closely.

As results from eqn. 4, the passage by diffusion may be represented by:

$$a_j i = D_i \left[ \frac{\partial C_i}{\partial x} \right] n_i F y \quad (29)$$

(in this expression the minus sign has been omitted because the cathodic current is regarded as positive in polarography). The differential quotient  $\partial C_1/\partial x$  is obtained by differentiation of eqn. 10,  $\partial C_2/\partial x$  and  $\partial C_3/\partial x$  by differentiation of eqn. 18.

The total current density  $i_j$ , which is obviously independent of  $x$ , is coupled with the deposition of the zinc ions supplied to the surface of the electrode. It may be assumed that in view of its relatively low concentration, the migration of the zinc ion makes no appreciable contribution.

$$i_j = {}^0j_1 = {}^0a_j = D_1 \left[ \frac{\partial C_1}{\partial x} \right] n_1 F y \quad (30)$$

The total part of the current density which is due to migration may be represented by:

$$m_j = i_j - \sum_a j_a \quad (31)$$

Practically only the ions of the supporting electrolyte contribute to the migration, so that:

$$m_j = m_j^2 + m_j^3 \quad (32)$$

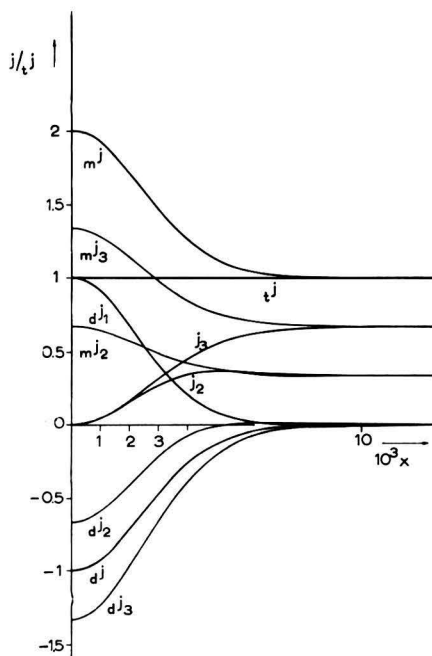


Fig. 2. Relative contributions to the electrolysis current as function of the distance from the electrode when supporting electrolyte is present.

As can be inferred from eqn. 4, the following also holds good:

$$mj_2 : mj_3 = C_2 D_2 : C_3 D_3$$

or, in view of the relatively small difference between  $C_2$  and  $C_3$ :

$$mj_2 : mj_3 = D_2 : D_3 \quad (33)$$

Combination of (32) and (33) gives us the values for  $mj_2$  and  $mj_3$ .

It has been shown above how the quantities  $\epsilon j$ ,  $aj_1$ ,  $aj_2$ ,  $aj_3$ ,  $aj$ ,  $mj$ ,  $mj_2$ , and  $mj_3$  can be calculated. In Fig. 2 each of these has been plotted as a function of the distance from the electrode, by which means the complicated joint action of the various forces on the ions present in the diffusion layer is illustrated in a clear and convenient way.

#### METAL DEPOSITION IN THE ABSENCE OF SUPPORTING ELECTROLYTE

The absence of supporting electrolyte simplifies the problem considerably. The starting-point is eqn. 6; it is not possible to neglect any terms in this. We shall replace  $i$  by  $I$  and  $z$  in eqn. 6:

$$\frac{\partial C_1}{\partial t} = D_1 \frac{\partial^2 C_1}{\partial x^2} + \frac{n_1 F y}{RT} D_1 \frac{\partial C_1}{\partial x} \frac{\partial E}{\partial x} + \frac{n_1 F y}{RT} D_1 C_1 \frac{\partial^2 E}{\partial x^2} \quad (34)$$

$$\frac{\partial C_3}{\partial t} = D_3 \frac{\partial^2 C_3}{\partial x^2} - \frac{n_3 F y}{RT} D_3 \frac{\partial C_3}{\partial x} \frac{\partial E}{\partial x} - \frac{n_3 F y}{RT} D_3 C_3 \frac{\partial^2 E}{\partial x^2} \quad (35)$$

The equation for electroneutrality now becomes:

$$n_1 C_1 = n_3 C_3 \quad (36)$$

If we introduce eqn. 36 into 35, we find:

$$\frac{n_1}{n_3} \frac{\partial C_1}{\partial t} = \frac{n_1}{n_3} D_3 \frac{\partial^2 C_1}{\partial x^2} - \frac{n_1 F y}{RT} D_3 \frac{\partial C_1}{\partial x} \frac{\partial E}{\partial x} - \frac{n_1 F y}{RT} D_3 C_1 \frac{\partial^2 E}{\partial x^2} \quad (37)$$

Multiplication of eqn. 37 by  $D_1$  and of eqn. 34 by  $D_3$ , followed by summation, gives rise to the elimination of the terms with  $\partial E/\partial x$  and  $\partial^2 E/\partial x^2$ :

$$\left( \frac{n_1}{n_3} D_1 + D_3 \right) \frac{\partial C_1}{\partial t} = \left( \frac{n_1}{n_3} + 1 \right) D_1 D_3 \frac{\partial^2 C_1}{\partial x^2}$$

or

$$\frac{\partial C_1}{\partial t} = \frac{n_1 + n_3}{n_1 D_1 + n_3 D_3} D_1 D_3 \frac{\partial^2 C_1}{\partial x^2} \quad (38)$$

In eqn. 38 the coefficient of  $\partial^2 C_1/\partial x^2$  represents the diffusion constant of the salt:

$$D_s = \frac{n_1 + n_3}{n_1 D_1 + n_3 D_3} D_1 D_3 \quad (39)$$

The solution of eqn. 38 is known from polarography:

$$C_1 = *C_1 \frac{2}{\sqrt{\pi}} \int_0^{\frac{x}{\sqrt{4D_s t}}} e^{-p^2} dp \quad (40)$$

The functions for  $C_1$  and  $C_3$  are indicated by dotted lines in Fig. 1.

The current density due to the diffusion of the zinc ion follows again from eqn. 4:

$$a_{j1} = n_1 F y D_1 \frac{\partial C_1}{\partial x} = n_1 F y D_1 \frac{C_1^*}{\sqrt{\pi D_1 t}} e^{-x^2/4D_1 t} \quad (41)$$

For the anion we have:

$$a_{j3} = -n_1 F y D_3 \frac{C_1^*}{\sqrt{\pi D_3 t}} e^{-x^2/4D_3 t} \quad (42)$$

The total current density  $i_j$  is determined by the sum of the migration part and the diffusion part of the cation at the surface of the electrode, *i.e.*:

$$i_j = \overset{\circ}{a}j_1 + \overset{\circ}{m}j_1 \quad (43)$$

$\overset{\circ}{a}j_1$  is known from eqn. 41;  $\overset{\circ}{m}j_1$  is derived from eqn. 4:

$$\overset{\circ}{m}j_1 = \overset{\circ}{C}_1 D_1 \frac{n_1^2 F y^2}{RT} \left[ \frac{\partial E}{\partial x} \right] \quad (44)$$

If we realize that at the cathode no electrochemical reaction of the anion takes place, we may write  $\overset{\circ}{j}_3 = 0$  or, subject to eqns. 4 and 36:

$$\frac{n_1}{n_3} \left[ \frac{\partial C_1}{\partial x} \right] = \overset{\circ}{C}_1 \frac{n_1 F y}{RT} \left[ \frac{\partial E}{\partial x} \right] \quad (45)$$

Substitution of (45) in (44) gives:

$$\overset{\circ}{m}j_1 = \frac{n_1^2}{n_3} D_1 F y \left[ \frac{\partial C_1}{\partial x} \right] \quad (46)$$

If we now compare  $\overset{\circ}{m}j_1$  and  $\overset{\circ}{a}j_1$  (see eqn. 41), it appears that:

$$m j_1 = \frac{n_1}{n_3} \overset{\circ}{a}j_1 \quad (47)$$

By replacing  $\overset{\circ}{m}j_1$  from eqn. 43 by eqn. 47, we find:

$$i_j = \left( 1 + \frac{n_1}{n_3} \right) \overset{\circ}{a}j_1 = (n_1 + n_3) \frac{n_1}{n_3} F y D_1 \frac{C_1^*}{\sqrt{\pi D_1 t}} \quad (48)$$

From the relation:

$$i_j = a_{j1} + a_{j3} + m_{j1} + m_{j3} \quad (49)$$

together with the eqns. 41 and 42, it follows that we are now able to calculate  $m_{j1}$  and  $m_{j3}$  for any value of  $x$ , because the ratio between these terms is also known, *viz.*:

$$m_{j1} : m_{j3} = n_1 D_1 : n_3 D_3 \quad (50)$$

Fig. 3 shows how the passage of the current through the diffusion layer is constituted in this case.

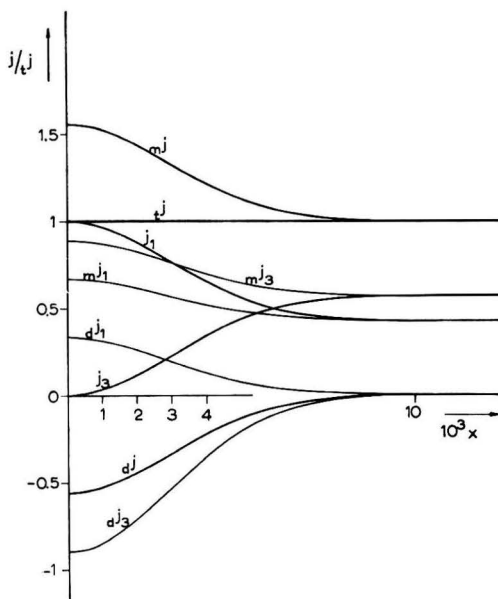


Fig. 3. Relative contributions to the electrolysis current as function of the distance from the electrode when no supporting electrolyte is added.

#### INFLUENCE OF THE SUPPORTING ELECTROLYTE ON THE VALUE OF THE LIMITING CURRENT

From what precedes it can be inferred at once how much the limiting current is increased when the supporting electrolyte is omitted. Division of eqn. 48 by eqn. 30 yields this ratio  $V$ :

$$V = \frac{(n_1 + n_3)}{n_3} \sqrt{\frac{D_1}{D_3}} \quad (51)$$

or, after introduction of eqn. 39:

$$V = \sqrt{\frac{n_1 + n_3}{n_3} \frac{n_1 D_1 + n_3 D_3}{n_3 D_3}} \quad (52)$$

The equation due to ILKOVIČ<sup>2</sup>, written in our nomenclature is:

$$V = \frac{n_1 D_1 + n_3 D_3}{n_3 D_3}$$

It is thus not correct.

KOLTHOFF AND LINGANE<sup>7</sup> made an amendment; their result is perfectly identical with eqn. 52. This is also the case with the relation derived by MACGILLAVRY<sup>8</sup>,



provided it is assumed that the diffusion coefficient  $D_1$  and the dropping time are not affected by the addition of supporting electrolyte.

In addition to this it may be useful to remark that in the absence of supporting electrolyte the well-known equation of continuity<sup>9</sup>:

$$D_{Ox} \left[ \frac{\partial C_{Ox}}{\partial x} \right] = D_R \left[ \frac{\partial C_R}{\partial x} \right]$$

should be replaced on account of eqn. 48 by:

$$\frac{n_{Ox} + n_3}{n_3} D_{Ox} \left[ \frac{\partial C_{Ox}}{\partial x} \right] = D_R \left[ \frac{\partial C_R}{\partial x} \right]$$

whilst  $\left[ \frac{\partial C_{Ox}}{\partial x} \right]$  is equal to  $*C_{Ox} / \sqrt{\pi D_{Ox} t}$  instead of to  $*C_{Ox} / \sqrt{\pi D_{Ox} t}$ .

#### ACKNOWLEDGEMENT

I am much indebted to the Institute for Applied Mathematics of this University for providing me with the solution of eqn. 17 and to IR. C. I. MOORING for his interest.

#### SUMMARY

In the above pages, a derivation has been given for the course of the concentration in a diffusion layer, which holds good for a flat electrode, with the exclusion of convection. Furthermore the transfer of the ions can be illustrated graphically, in the presence as well as in the absence of supporting electrolyte.

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# EFFECT OF THE DOUBLE LAYER STRUCTURE AND OF THE ADSORPTION OF ELECTRODE REACTION PARTICIPANTS UPON POLAROGRAPHIC WAVES IN THE REDUCTION OF ORGANIC SUBSTANCES

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## INTRODUCTION

The effect of the double layer structure on the kinetics of electrochemical processes was first noted by FRUMKIN in developing the theory of slow discharge and hydrogen overvoltage<sup>1,2</sup>. Later on FRUMKIN'S concepts were successfully applied by himself and his co-workers for explaining phenomena occurring in the electro-chemical reduction of oxygen<sup>3</sup>, anions<sup>4-9</sup>, and a number of other electrode processes. The ideas of FRUMKIN are now widely known (see, *e.g.*, refs.<sup>10-12</sup>); a number of works have appeared concerned with the effect of the double layer structure on electrode processes controlled by the kinetics of preceding chemical reactions<sup>13-16</sup>.

The adsorption on the electrode of neutral organic molecules<sup>17</sup>, particularly of components of chemical reactions preceding the electron transfer, also exhibits a marked effect on the kinetics of electrode processes. Regularities of molecular adsorption and its relation to various factors, in particular to the electrode potential, were first established also by FRUMKIN<sup>18</sup> (see also ref. <sup>19</sup>).

The present work is concerned with the effects of the double layer structure and the adsorption of electrode reaction components on kinetics of different electrode processes involving organic compounds, illustrated with polarographic waves.

## EXPERIMENTAL

The experimental results discussed in this work were obtained by means of a polarograph ДЭ-312 with potentiometric control of the dropping electrode potential (accurate to within  $\pm 2$  mV)<sup>20</sup>. The preferred electrode for use was one with a small glass beak for forced detachment of drops (completely eliminating oscillations of the current and variations in the drop time with the potential). It had the following characteristics:  $m = 1.02$  mg/sec,  $t = 0.23$  sec. The work was carried out in a thermostatted cell<sup>21</sup> at  $25 \pm 0.2^\circ$ . Correction for residual current was made by recording curves for supporting electrolytes. To remove atmospheric oxygen all solutions were deaerated with nitrogen.

The solutions investigated contained only 1:1-charged electrolytes. One set of

experiments involved variations in ionic strength (addition of KCl) at strictly constant pH and buffer capacity; the other — variations in the buffer capacity at constant pH (more precisely  $\text{p}a\text{H}$ ) and ionic strength.

#### IRREVERSIBLE pH-INDEPENDENT WAVES OF UNCHARGED SUBSTANCES

In this case the effect of the double layer structure is confined to a change in the effective potential difference between the electrode and the particle under discharge determining the rate of electron transfer. The effective potential difference is lower than the overall potential difference between the electrode and a sufficiently removed point in the body of the solution, by a value of  $\psi_1$  corresponding to the potential drop in the diffuse part of the double layer<sup>1,2</sup>. With solutions of 1:1-charged electrolytes and in the absence of specific adsorption the  $\psi_1$  value will be fairly accurately described by<sup>22</sup>:

$$\varphi_a = \psi_1 + \frac{1}{C} \sqrt{\frac{2DRTc}{\pi}} \operatorname{sh} \left( \frac{\psi_1 F}{2RT} \right) \quad (1)$$

here  $\varphi_a$  is the electrode potential relative to the electro-capillary zero point,  $C$  the integral capacity of the double layer,  $D$  the dielectric constant of the solution,  $c$  the overall (molar) concentration of 1:1-charged electrolytes. With potentials sufficiently removed from the zero-point charge,  $\psi_1$  will be given by the approximate equation

$$\psi_1 \approx \text{const} + \frac{RT}{F} \ln c - \frac{2RT}{F} \ln \varphi_a \quad (2)$$

With aqueous solutions at 25°, when  $c$  is expressed in M/l,  $\text{const} \approx -0.06$  V.

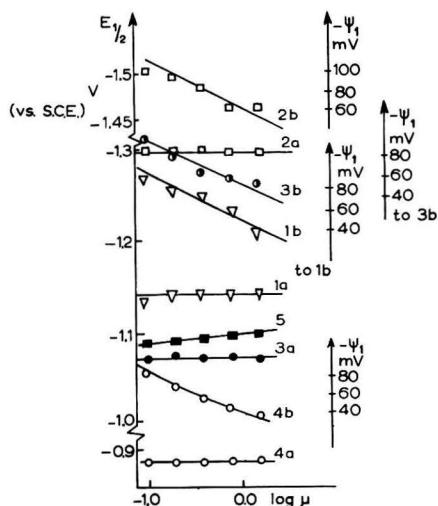


Fig. 1. Points correspond to  $E_{1/2}$  values for waves of the reduction of: benzaldehyde (1), acetophenone (2), 2-acetothiophenylaldehyde-4 (3), 2,2'-dithiophenylketone (4), semicarbazone 2-acetylthiophene (5), at different ionic strengths of the acetate buffer solution ( $\sim 0.1$  M  $\text{CH}_3\text{COOH} + 0.1$  M  $\text{CH}_3\text{COOK} + \text{KCl}$ ) and  $\text{pH} = 4.65$ : (a)  $E_{1/2}$  of first waves, (b) of second waves. Curves denoted by "b" correspond to variation of  $\psi_1$  with concentration of  $\text{K}^+$  (the scale for  $\psi_1$  is given to the right of the curves).

LEVIN AND FODIMAN were the first to associate the variation of  $E_{1/2}$  of the reduction of halogen derivatives with the composition of the supporting electrolyte<sup>23</sup>. Later on, the effect of  $\psi_1$  on  $E_{1/2}$  (and also on the slope of logarithmic plots of waves) was investigated by ROGERS *et al.*<sup>11</sup>. Quantitative studies of the effect of potassium chloride concentration on  $E_{1/2}$  of the reduction of certain organic iodine derivatives showed that  $E_{1/2}$  actually varies almost directly with the  $\psi_1$ -potential<sup>24</sup>.

The points on curves 1-4 in Fig. 1 represent  $E_{1/2}$  values of first (a) and second (b) waves of reduction of benzaldehyde (1), acetophenone (2), 2-acetothiophenaldehyde-4 (3), and 2,2'-dithiophenylketone (4) in an acetate buffer of pH = 4.65 and  $[\text{CH}_3\text{COOH}] \approx 0.1 M$  at a different ionic strength (0.1 M  $\text{CH}_3\text{COOK} + \text{KCl}$ ). Second waves correspond to irreversible reduction of free radicals without the participation of hydrogen ions in the potential-determining step<sup>25,26</sup>. As is consistent with the theory,  $E_{1/2}$  becomes more positive with increasing ionic strength of the solution. Curves 1(b) to 4(b) in Fig. 1, plotted from eqn. 1 under the assumption that  $C = 18 \mu\text{F}/\text{cm}^2$ ,  $D = 78$  and the potential of the electrocapillary maximum is  $-0.45 V$  vs. S.C.E., illustrate the variation of  $\psi_1$ -potential with increasing concentration of salts. The variation of  $E_{1/2}$  is seen to be fairly consistent with that of the  $\psi_1$ -potential (Fig. 1) (the low value of the liquid junction variation will be disregarded here and hereafter).

It will be noted that with  $c_{\text{KCl}} < 0.1 M$  the second wave of acetophenone is almost completely masked on polarograms by the discharge current of the supporting electrolyte. With increase in  $c_{\text{KCl}}$  it is shifted to positive potentials and becomes easily detectable. For benzaldehyde the increase in  $c_{\text{KCl}}$  results in the merging of the second and first waves and, consequently, at  $c_{\text{KCl}} \geq 0.3 M$  the values of  $E_{1/4}$  and  $E_{3/4}$  of the composite wave were taken as those for  $E'_{1/2}$  and  $E''_{1/2}$ , respectively, since the heights of the first and second benzaldehyde waves were equal.

#### POLAROGRAPHIC WAVES WITH PRE-PROTONATION

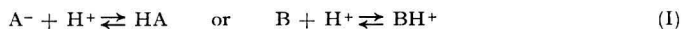
This section deals with processes in which the limiting currents are controlled by the rate of the preceding chemical reaction (kinetic and catalytic waves) and processes, where the preceding reaction affects the rate of the electrochemical step (or roughly speaking, the  $E_{1/2}$  of waves).

##### (a) Variation of pH in the electrode region as compared with the bulk of the solution

The double layer structure exerts an important effect on the distribution of charged particles in the vicinity of the electrode surface. The concentration of hydrogen ions and other positively charged acid components of buffer solutions is higher at the electrode surface than in the bulk of the solution, while the concentration of negatively charged bases is lower at the cathode surface. Variation of ion concentrations close to the electrode surface in the absence of specific adsorption obeys the Boltzmann distribution. Thus the concentration of cations and anions in the immediate vicinity of the electrode surface will be<sup>22</sup>

$$[\text{BH}^+]_s = [\text{BH}^+]_o e^{-\psi_1 F/RT}, \quad [\text{A}^-]_s = [\text{A}^-]_o e^{\psi_1 F/RT} \quad (3)$$

where s and o indexes define concentrations close to the electrode surface and in the bulk of the solution, respectively, and  $\text{BH}^+$  is any cationic acid, including hydroxonium ions. For an acid-base system



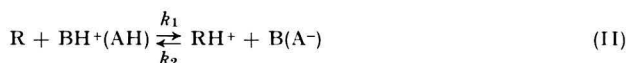
where  $A^-$  is any anion, including  $OH^-$ , and  $B$  is the uncharged base, in particular water; this may be written

$$\left(\frac{[HA]}{[A^-]}\right)_s : \left(\frac{[HA]}{[A^-]}\right)_o = \left(\frac{[BH^+]}{[B]}\right)_s : \left(\frac{[BH^+]}{[B]}\right)_o = \frac{[H^+]_s}{[H^+]_o} = e^{-\psi_1 F/RT} \quad (4)$$

since for uncharged particles in the absence of specific adsorption  $[HA]_o = [HA]_s$  and  $[B]_s = [B]_o$ .

Thus, as the charge of the acid components of the buffer system is always above that of conjugated bases, the acid-base equilibrium close to the cathode surface will always be shifted towards the acid form, compared with the bulk of the solution<sup>27</sup>. This shift may amount to quite considerable values. Thus, for  $\psi_1 \approx -120$  mV, which takes place, for instance, in a 0.1 M solution of 1.1-charged electrolyte at an electrode potential of  $E \approx -1.5$  V vs. S.C.E., the pH at the electrode surface will be more than two units lower than in the bulk of the solution.

For electrode processes preceded by a chemical protonation reaction,



a decrease in pH at the electrode surface results in an increased rate of protonation ( $k_1 - k_2$ ) of the electrochemically inactive (at the given potential) substance  $R$ , which is converted in this way into an electrochemically active cationic form of  $RH^+$ . The greatest shift of pH and, consequently, the highest increase in the protonation rate, will occur in the thin layer immediately adjacent to the electrode. With expansion of the layer in which the protonation reaction (II) takes place, the double layer structure effect will become less marked<sup>10,14,15</sup>. Indeed, it was shown for catalytic waves of hydrogen in pyridine solutions<sup>28</sup>, for which the preceding protonation (II) occurs in the reaction zone of the solution close to the electrode surface, that a decrease in the reaction layer thickness leads to an appreciable increase in the apparent rate of protonation<sup>28</sup>. The greatest effect of the pH shift in the electrode-surrounding layer is observed<sup>27</sup> for the so-called "surface" kinetic and catalytic waves<sup>29,30</sup>, for which the preceding reaction occurs on the electrode surface proper, with participation of adsorbed substances. In this (and only in this) event the pH shift in the reaction layer may be accounted for by eqn. 4<sup>27</sup>. It will be noted that the effect of the ionic strength of a buffer on the kinetic current with pre-protonation was first discussed in terms of the  $\psi_1$ -potential variation by GRABOWSKY AND BARTEL<sup>13</sup>. The results obtained by these investigators were in good quantitative agreement with theory, due to the "surface" nature of the process they studied.

#### (b) *Pre-protonation in electrochemical reduction of organic substances*

The reduction of organic substances involving retarded electron transfer and the participation of protons in the potential determining step seems to proceed by schemes (II)–(III), *i.e.* with pre-protonation: simultaneous addition of a proton and an electron is scarcely possible for such processes. Indeed, for an acid medium, the transition of a substance to the protonated form before an electron is taken up occurs in

the reduction of: aldehyde and ketone derivatives at the carbonyl group<sup>31,32</sup>, nitrosamines<sup>33</sup>, sydnone<sup>34</sup>, nitrocompounds<sup>35,36</sup>, thiobenzamide derivatives<sup>37</sup>, acid amides<sup>38</sup>, N-oxides of amines<sup>39</sup>, azulene<sup>40</sup>, tropolone<sup>41,42</sup>, tropone<sup>42</sup>, cyclopentadienylide of pyridinium and guaiazulene<sup>43</sup>, various pyridine derivatives<sup>44</sup>, azobenzene<sup>45</sup>, ketosteroids<sup>45a</sup>, and many other compounds.

Our experimental results provide confirmation of the occurrence of pre-protonation. With increase in concentration of non-dissociated acetic acid from 0.1 *M* to 0.4 *M* in an acetate buffer of pH = 4.65 = const. at a constant ionic strength = 0.5 *M* (replacement of KCl with CH<sub>3</sub>COOH and CH<sub>3</sub>COOK, and pH brought up to 4.65)  $E_{1/2}$  of the reduction of semicarbazone 2-acetylthiophene (~0.5 mM) was shifted by ~18 mV towards positive potentials. The easier reduction of semicarbazone cannot be explained otherwise than by acceleration of its protonation, which occurs not only under the action of hydrogen ions, but also of non-dissociated CH<sub>3</sub>COOH. Pre-protonation of nitrocompounds was proved in the same way<sup>35</sup>; it was shown<sup>35</sup> that not only the buffer capacity, but, more so, the nature of the buffer acid is of importance in these cases.

In alkaline media for processes involving hydrogen ions  $E_{1/2}$  usually does not depend on pH. In this case pre-protonation may occur only due to the proton-donor properties of water. However, in alkaline media, especially so in aprotic solvents, another mechanism of electrode processes may occur, when there is first transfer of an electron and then the anion-radical formed abstracts the proton from water or the molecule of the organic solvent.

(c) "Surface" nature of protonation in electrode processes involving organic substances

It was already noted that the effect of the double layer structure is a maximum for protonation reactions occurring on the electrode surface and is practically absent in reactions proceeding in a fairly thick layer ("space" reactions). Let us show that the protonation of many organic compounds involves adsorbed particles, *i.e.* occurs in the surface layer.

Protonation of a strictly "space" nature, proceeding in the reaction layer<sup>46,47</sup> of a thickness about 50 Å, will be considered. When there is no appreciable concentration polarisation and the concentration of the depolarizer in the R form (scheme II) is about 0.5 mM/l, the amount in the reaction layer per 1 cm<sup>2</sup> of the electrode surface will be  $5 \cdot 10^{-7} \text{ cm} \times 1 \text{ cm}^2 \times 5 \cdot 10^{-7} \text{ M cm}^{-3} = 2.5 \cdot 10^{-13} \text{ gmole}$ .

An overwhelming majority of organic substances are surface-active at the mercury-water interface (see, *e.g.*, ref.<sup>48</sup>), *i.e.* are adsorbed at the mercury surface. Let us assume that the adsorption of substance R is relatively weak, so that under experimental conditions the electrode surface coverage with adsorbed R will be ~0.5% only. It will be noted that this low extent of adsorption corresponds to potentials lying considerably beyond the so-called "desorption peak"<sup>22</sup> and, consequently, its value cannot be determined using conventional methods (measurement of surface tension, of the double layer capacity, etc.). Even for this weak adsorption and using the assumption that  $\Gamma_{\infty} = 5 \cdot 10^{-10} \text{ gmole/cm}^2$  ( $\Gamma_{\infty}$  is the maximum amount of adsorbed substance at a complete monolayer coverage of the surface), the amount of adsorbed R per 1 cm<sup>2</sup> will be  $2.5 \cdot 10^{-12} \text{ gmole}$ , *i.e.* by an order higher than in the "space" reaction layer. If the rate constants of "space" protonation and of protonation at the electrode surface are assumed to be of the same order, and allowing for the

fact that the concentration of proton donors close to the electrode surface is higher than in the bulk of the solution, the protonation process (II) will obviously proceed mainly at the electrode surface, even in the relatively unfavourable case of weak adsorption considered above. It follows from the above that the majority of electrode processes preceded by a chemical reaction involving organic substances will be of a strictly "surface" nature.

In considering both kinetic and catalytic polarographic waves, the discovery and theoretical substantiation of which are to the merit of BRDIČKA and co-workers (see *e.g.*, ref.<sup>49</sup>) it was equally necessary to allow for the "surface" nature of many processes<sup>29,30</sup>. If the adsorption effect is not allowed for, the rate constants of many fast reactions, derived from polarographic data, will appear to be too high<sup>29,30</sup> (see also<sup>50</sup>).

The higher rate of "surface" processes (due to higher concentrations of reactants in the reaction zone), as compared with "space" processes, accounts, for instance, for the fact that "surface" kinetic currents of acids are observed even at pH's higher by 8-9 units than the  $pK_A$  of these acids<sup>39</sup>, and the so-called apparent "polarographic"  $pK'_A$ <sup>51,52</sup> may exceed the true  $pK_A$  values by more than 7 units. (For strictly "space" kinetic currents of acids at  $pK_A$  not lower than 1.0, the difference in  $pK_A$  and  $pK'_A$  cannot be above 4-5 units).

The sorbtivity of the preceding reaction components diminishes with increasing temperature and this makes up, to a certain extent, for the current rise due to increase in the reaction rate constant. This provides an explanation for the very small variation in kinetic currents with temperature<sup>9,53,54,55</sup> observed sometimes, and accounted for by the almost zero or even negative activation energy for the preceding reaction<sup>9,53,55</sup>. With a considerable increase in temperature, the amount of the reactant adsorbed may become so small, that the kinetic current will no longer become a "surface" but, rather, a "space" current. This was observed for the second wave of maleic acid controlled by the rate of monoanion protonation to non-dissociated acid: the almost temperature-independent (at low temperatures) apparent protonation rate constant began to increase appreciably at  $t^\circ > 70^\circ$ . This corresponds to increase with temperature of the rate constant of the "space" reaction, which prevails over the decrease in the overall reaction rate, caused by the desorption of maleic acid monoanions<sup>56</sup>.

#### (d) Effect of the double layer structure on ion discharge

When the particles discharged are ions, *i.e.* are positively or negatively charged, their concentration in the electrode-surrounding layer differs from that in the bulk of the solution, due to the electrostatic action of the electrode field (see eqn. 3). Besides influencing the effective potential difference, variations in the concentration of particles undergoing discharge close to the electrode surface also affect the rate of the electro-chemical process and, consequently, the  $E_{1/2}$  of irreversible polarographic waves. On the theory of slow discharge, the variation of  $E_{1/2}$  of pH-independent waves with the double layer structure may be written as

$$\Delta E_{1/2} \approx A\psi_1 \frac{\alpha n_a - z}{\alpha n_a} \quad (5)$$

where  $\alpha$  is the transfer coefficient ( $0 < \alpha < 1$ ),  $n_a$  the number of electrons transferred in the potential-determining step (usually  $n_a = 1$ ),  $z$  the charge of the particle being

discharged. It follows from eqn. 5 that for non-charged particles ( $z = 0$ )  $\Delta E_{1/2} \approx \Delta\psi_1$ , *i.e.* variation of  $E_{1/2}$  corresponds to the effective potential difference only, a case already discussed in the first section of this paper. The absolute value of  $z$  is higher than  $\alpha n_a$ , and consequently, in cation discharge ( $z > 0$ ) the signs of  $\Delta E_{1/2}$  and  $\Delta\psi_1$  will be opposite, *i.e.*  $E_{1/2}$  will become more negative with decrease in the absolute value of  $\psi_1$  due to a rise in the ionic strength. In the case of anions  $z < 0$  and  $(\alpha n_a - z)/\alpha n_a$  is positive and considerably above unity. Consequently, as is consistent with eqn. 5, a decrease in the absolute value of  $\psi_1$  results in a considerably greater shift of  $E_{1/2}$  to positive potentials. These conclusions are fully confirmed by experiment. Some examples of the effect of  $\psi_1$  variation on  $E_{1/2}$  of cationic and anionic discharge waves will be given below.

When the electrochemical step is preceded by a chemical reaction of first order with respect to the initial substance R, and of all the reagents only R is an ion, variation of R concentration in the electrode-surrounding layer under the influence of the electrode field will result in proportional variation of the concentration of the electrochemically active product formed by the chemical reaction and, consequently, of the electrode reaction rate. Thus, and in the case of electrode processes preceded by a chemical reaction involving ions as initial reactants, the double layer structure effect on  $E_{1/2}$  will also obey eqn. 5, and in this case  $z$  will be the charge of the electrochemically inactive substance R.

It will be noted that when a substance is present in the solution chiefly in a non-ionized state and its transition to the ionic form occurs only before the discharge on the electrode surface (as, for example, with "surface" protonation) the electrostatic field of the electrode will have no effect on the distribution of concentrations of this substance at the electrode, and thus  $z$  in eqn. 5 should be considered as zero.

Things become more complex when the preceding reaction is one between several ions or a protonation process. Pre-protonation will be considered in the next section.

(e) *Effect of the double layer structure on processes preceded by protonation*

The value of  $E_{1/2}$  for polarographic processes preceded by protonation becomes more negative with increase in pH in acid and neutral solutions, and as a rule

$$\frac{\partial E_{1/2}}{\partial \text{pH}} = -40 \div -80 \text{ mV/pH units}$$

Variation of pH at the electrode surface with the  $\psi_1$ -potential will affect also  $E_{1/2}$  of irreversible waves preceded by "surface" protonation. It may be readily shown from eqn. 4 that only a change in pH in the electrode-surrounding layer will lead to  $\Delta E_{1/2} = [(\partial E_{1/2})/\partial \text{pH}][(\Delta\psi_1 F)/2.3RT]$ . In a general case of irreversible ion discharge with "surface" pre-protonation it may be written

$$\Delta E_{1/2} \approx \Delta\psi_1 \left( \frac{\alpha n_a - z}{\alpha n_a} + \frac{\partial E_{1/2}}{\partial \text{pH}} \frac{F}{2.3RT} \right) \quad (6)$$

Eqn. 6 shows that in certain cases variation of the ionic strength will cause very considerable variation of  $E_{1/2}$ . Indeed, with a wave of N-methylpiperidine N-oxide, reduced in an acetate buffer of pH = 4.6, a ten-fold increase in the ionic strength (addition of NaCl) resulted in an almost 200 mV shift of  $E_{1/2}$  to negative potentials<sup>39</sup>.



This value is in good agreement with that calculated from eqn. 6, since in the given case  $z = 1$  ( $pK_A$  of methylpiperidine N-oxide is 5.12),  $\alpha n_a \approx 0.3$ ,  $\partial E_{1/2}/\partial pH \approx -60$  to 70 mV/pH units.

As stated before, for substances present in the solution in a non-ionic form, which is the case for the majority of organic compounds,  $z = 0$ . Taking into consideration that the value of the second term in brackets of eqn. 6 is close to  $-1$ , it may be readily shown from eqn. 6 that for waves of uncharged particles preceded by protonation  $E_{1/2}$  will be almost independent of  $\psi_1$  or of the ionic strength of the solution. Indeed, at constant pH and buffer capacity  $E_{1/2}$  for the semicarbazone 2-acetylthiophene reduction, for example, (Fig. 1, straight line 5) is almost independent of the ionic strength. Variation of the potential difference with  $\psi_1$  will practically cancel out the  $E_{1/2}$  shift caused by variation of pH at the electrode surface.

In certain particular cases, instead of cancelling out both effects may add up. This would probably occur in the reduction of nitromethane in an acid medium in the presence of iodine ions. Centres of adsorbed anions are nearer to the surface than those of cations and, consequently, it is necessary to distinguish between  $\psi_1$ -potentials corresponding to the inner ( $\psi_1^i$ ) and outer ( $\psi_1^o$ ) Helmholtz planes<sup>57</sup>. The shift in  $E_{1/2}$  of nitromethane with KI concentration was compared<sup>10</sup> with variations of  $\psi_1^i$  and  $\psi_1^o$ , the values of which for various potentials and several KI concentrations were calculated by GRAHAME<sup>58</sup>, who based his work on the theoretical concepts of ESIN, SHIKHOV AND ERSHLER<sup>59,60</sup>. Under conditions that were used in nitromethane polarography  $\psi_1^i$  became more negative and  $\psi_1^o$  more positive with rise in  $C_{KI}$ ; in absolute magnitude both  $\Delta\psi_1^i$  and  $\Delta\psi_1^o$  were approximately the same (*cf.* Fig. 6 in ref.<sup>10</sup>). The  $E_{1/2}$  shift observed was towards negative potentials and its value  $\Delta E_{1/2}$  was almost twice that of  $\Delta\psi_1^i$ <sup>10</sup>. It would be logical to infer, and this is done by the authors<sup>10</sup>, that the shift of  $E_{1/2}$  with variation of the effective potential difference is due to  $\Delta\psi_1^i$  and the rise of the  $\Delta E_{1/2}$  value over  $\Delta\psi_1^i$ , left unexplained<sup>10</sup>, may possibly be associated with increase in pH in the outer Helmholtz plane through a shift of  $\psi_1^o$  to positive values.

It will be noted that, as shown by our investigations<sup>61</sup>, variation of  $E_{1/2}$  of nitrocompound waves with the concentration of indifferent electrolytes is related mainly to variation of the effective potential difference; the pH variation in the electrode-surrounding layer is of less importance, probably due to the partly "space" nature of pre-protonation<sup>61</sup>.

Let us consider now the effect of the double layer structure on  $E_{1/2}$  of first aldehyde and ketone waves. For the compounds studied, the  $E_{1/2}$  of first waves in an acid medium at a pH maintained constant are practically independent of ionic strength (straight lines "a" in Fig. 1), or of the buffer capacity and the nature of buffer components, though  $E_{1/2}$  will become more negative with increase in pH, approximately by  $-60$  mV/pH units. This behaviour may find its explanation only in the reversibility of the electrode process<sup>25,26,62-64</sup>, in which case  $E_{1/2}$  will be determined not by the rate of protonation and of the following electrode reaction, but by electrochemical equilibrium between R and R<sup>-</sup> (occurring with direct transfer of the electron to R) and RH<sup>+</sup> and RH, and by their protolytic equilibrium with hydrogen ions in solutions.

It follows that the absence of effect of the ionic strength and buffer capacity on  $E_{1/2}$  may in many cases be considered as a criterion for the reversibility of electrode processes.

The double layer structure exerts an effect also on kinetic and catalytic waves controlled by the rate of "space" pre-protonation when the latter proceeds in the sufficiently thin electrode-surrounding layer<sup>10,14,15,28</sup>, where the mean pH value appreciably differs from that of the bulk of the solution. The limiting strictly "space"<sup>65</sup> catalytic current of hydrogen caused by pyridine in a borate buffer ( $\text{KH}_2\text{BO}_3 + \text{H}_3\text{BO}_3$ ) of  $\text{pH} = \text{const} = 8.00$ , as a function of the ionic strength (addition of KCl) is shown as an example in Fig. 2. With increasing KCl concentration  $\psi_1$  decreases, pH becomes higher in the vicinity of the electrode and this results in diminution of the catalytic wave height.

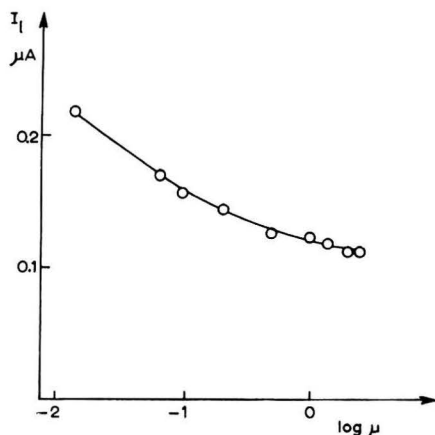


Fig. 2. The height of a catalytic hydrogen wave in the presence of 0.11 mM pyridine in a borate solution of  $\text{pH} = 8.00$  at constant buffer capacity as a function of the ionic strength (addition of KCl).

The effective thickness of the diffuse part of the double layer diminishes with the rise in ionic strength and becomes considerably less than the thickness of the reaction layer, so that at relatively high KCl concentrations its effect on catalytic waves becomes less marked (Fig. 2).

#### VARIATIONS IN POLAROGRAPHIC WAVES RELATED TO THOSE IN THE SORBTIVITY OF COMPONENTS OF THE CHEMICAL REACTION PRECEDING ELECTRODE PROCESSES

The theory of adsorption of uncharged molecules at the electrode-solution interface was developed by FRUMKIN<sup>18</sup>. Strongest adsorption occurs at the so-called maximum adsorption potential ( $E_M$ ) close to the electrocapillary zero-point<sup>18,19</sup>. Variation of the electrode potential with respect to  $E_M$  (either towards the cathode, or anode) brings about a fall in sorbtivity, as shown by a bell-shaped curve. When adsorption obeys the LANGMUIR isotherm

$$\Gamma_e = \Gamma_\infty \frac{\beta C_k}{1 + \beta C_k} \quad (7)$$

( $\Gamma_e$  is the equilibrium amount of the adsorbed substance, and  $C_k$  the concentration

in the bulk of the solution, variation of factor  $\beta$  with the potential may be expressed by FRUMKIN's equation<sup>18</sup>

$$\beta = \beta_0 e^{-\frac{C-C'}{2RT\Gamma_\infty} \varphi^2} \quad (8)$$

Here  $\varphi = E - E_M$ , *i.e.* it represents the potential measured with respect to  $E_M$ ;  $C$  and  $C'$  denote the specific capacity of the double layer of the electrode in the absence of a surface-active substance and at complete coverage of the electrode surface by adsorbed molecules. Under conditions which usually occur in polarography, equilibrium adsorption does not begin on the dropping electrode, and the actual amount of adsorbed substance  $\Gamma_t$  is less than that at equilibrium<sup>66</sup>

$$\Gamma_t = y\Gamma_e \quad (9)$$

( $y \leq 1$  is a function of the adsorption time and of  $\beta C_k$ <sup>66</sup>).

In accordance with eqns. 7 and 8, the amount of substance adsorbed varies directly with the potential. However, adsorption of many compounds obeys not the LANGMUIR, but the FRUMKIN S-shaped isotherm<sup>67,68,69</sup>; in this case desorption with potential variation may occur sharply, jump-wise. For small coverage of the electrode surface, usual in polarography, the adsorption isotherm of FRUMKIN practically coincides with that of LANGMUIR. Consequently, combined use of eqns. 6 to 9 would be justifiable for the majority of cases.

The effect of concentration of indifferent electrolytes on the sorptivity of some substances depends upon the change in  $C$  in eqn. 8: increase in the salt concentration leads to increasing  $C$  and thus to weaker sorptivity and more rapid desorption with the potential rise.

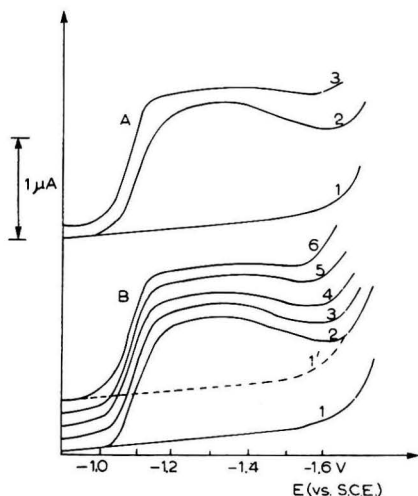


Fig. 3. Polarographic waves of 2-acetylthiophene semicarbazone reduction ( $4.0 \cdot 10^{-4}$ ) in acetate buffers ( $\text{CH}_3\text{COOH} + \text{CH}_3\text{COOK} + \text{KCl}$ ) at  $\text{pH} = 4.65$ : A, ionic strength = const =  $0.5$ , concentration of  $\text{CH}_3\text{COOH} = (2) 0.1 M, (3) 0.4 M$ ; B, constant concentration of  $\text{CH}_3\text{COOH} (\sim 0.1 M)$ , ionic strength = (2)  $1.6, (3) 0.8, (4) 0.4, (5) 0.2, (6) 0.1 M$ ; I and I' the supporting electrolyte curves at an ionic strength of  $1.6 M$  and  $0.1 M$ , respectively.

Variation of the sorbtivity with the potential is most marked for waves, the heights of which are controlled by the preceding chemical reaction involving adsorbed components. Desorption of R (see scheme II) with the potential rise will then involve diminution of wave heights, in particular of "surface" catalytic hydrogen waves<sup>70</sup> (a quantitative description of the wave form was made from eqns. 7 and 8<sup>70</sup>), or of "surface" kinetic waves, for instance of weak acids, and in polarograms of azomethine derivatives, under conditions when the kinetic current becomes lower than the diffusion current<sup>31,32</sup>. The limiting kinetic current is controlled by the protonation rate  $k_1$  of the surface-adsorbed basic form R, such as anion acids or the base of an azomethine derivative. Consequently, its value will be affected<sup>29</sup> both by the amount of adsorbed base  $\Gamma_R$  and the concentration of proton donors  $BH^+$  (or  $AH$ ) accounting for the formation of the acidic electrochemically active form (scheme II). Polarograms for a compound involving an azomethine group, 2-acetylthiophene semicarbazone, are shown in Fig. 3 for two sets of experiments: A — at constant ionic strength and pH, but at different buffer capacities ( $C_{CH_3COOH}$  0.1 and 0.4 M, respectively) and B — at constant pH and buffer capacity, but different ionic strengths. A fall of current on the limiting plateau, due to desorption of semicarbazone to an extent making the protonation-controlled kinetic current value lower than that of the diffusion current, is observed on all polarograms of Fig. 3. With increase in the buffer capacity, *i.e.* in the protonation rate, the fall becomes less, while with increase in the ionic strength, resulting in a rise of pH in the electrode-surrounding layer and diminishing of the semicarbazone sorbtivity, the fall becomes greater. A similar effect of the buffer capacity and the ionic strength is observed for "surface" catalytic waves of hydrogen<sup>70,27</sup>.

In certain cases (at a time considerably in advance of that corresponding to attainment of adsorption equilibrium) the amount of substance R adsorbed increases with the time of adsorption<sup>71,66</sup>, *i.e.* there is an increase in the degree of equilibrium attainment ( $y$ ) in eqn. 9. This leads to a rise of the current limited by the preceding "surface" reaction with a longer drop time<sup>29,72-74</sup>. The greater amount of adsorbed azobenzene might also serve as an explanation for the apparent increase with time of the rate constant for a protolytic reaction between chloroacetic acid and azobenzene<sup>75</sup>, as determined by the potentiostatic method using the RÜETSCHI procedure<sup>45</sup>.

A gradual decrease in the amount of the substance adsorbed with variation of the potential within the wave range may also be the reason for the less steep polarographic wave<sup>70</sup>. Thus, when the true slope in the logarithmic plot of the wave corresponding to the electrochemical reaction proper in the discharge of anabasine and quinine (under conditions of catalytic hydrogen evolution) is about 70 and 85 mV, respectively, the observed slope accounted for by desorption of these products<sup>70</sup> will be close to 100 mV.

Variation of the nitromethane wave slope<sup>76</sup> with increase in pH of the solution (and, consequently, with a shift of the wave to the negative potential range) seems to be also related in part to nitromethane desorption. The  $E_{1/2}$  value for nitromethane as a function of pH is represented by an S-shaped curve<sup>76</sup>. Protonated nitromethane will be reduced in strongly acidic solutions<sup>35</sup> and unprotonated nitromethane in a neutral medium, while in weakly acidic solutions there will probably be a combined wave for both forms. At a pH > 5.0 the wave slope practically attains the highest constant value<sup>76</sup>. It may be assumed that, in this case, the pre-protonation of nitro-

methane (which seems to occur u8p) ece =ptpo oHo.or ds only in the bulk of the solution, due to desorption, and the observed value of  $\alpha n_a = 0.97^{76}$  apparently coincides with its true value. In acid solutions reduction occurs at less negative potentials and some adsorption of nitromethane, consequently, takes place, so that in the course of recording the wave the amount of the substance adsorbed will decrease with increasing cathode potential. This would lead to a decrease in the protonation rate, an increase in the fraction of unprotonated-form in the overall amount of the substance under discharge and to a resulting shift in potentials of the upper wave parts towards the cathode region. The wave slope becomes less steep, which causes a considerable drop in the apparent  $\alpha n_a$  value. With a strongly acidic medium there is an inflexion in the logarithmic plots at  $E \approx -0.65$  V vs. S.C.E.: the upper parts of the waves have a more gradual slope than the lower ones<sup>76</sup>. This is again due to desorption of nitromethane becoming appreciable at  $-0.65$  V only.

The unusual variation of the wave with temperature is evidence that nitromethane adsorption actually plays a part in its reduction. The wave slope for irreversible processes should be independent of temperature, and the  $\Delta E_{1/2}/\Delta t^\circ$  ratio should be positive. For nitromethane waves  $\Delta E_{1/2}/\Delta t^\circ$  is negative at pH = 4.3 and the wave slope increases with temperature<sup>76</sup>. These facts may find an explanation in desorption of nitromethane with temperature and the corresponding sharp decrease in the rate of its protonation, resulting, as shown before, in a shift of  $E_{1/2}$  towards the cathode and a rise in the  $\alpha n_a$  value observed. A greater slope of the nitromethane wave, observed with rise of the salt concentration (*i.e.* with decrease in the absolute value of  $\psi_1$ )<sup>10</sup> may also be explained by a fall in the protonation rate and decrease in sorbtivity with higher ionic strength.

#### ELECTRODE PROCESSES ON THE CATHODE, INVOLVING ANIONS

A rise of the indifferent electrolyte concentration in the solution diminishes the repulsion of anions from the negatively charged cathode surface and thus favours their reduction<sup>4-9,77-79</sup>. It was already noted that in the discharge of anions the  $z$  value will be negative, the value of  $(\alpha n_a - z)/\alpha n_a$  positive and above unity. Consequently, and in accordance with eqn. 6, a decrease in the absolute  $\psi_1$  value will result in a shift of  $E_{1/2}$  to positive potentials, and when  $\partial E_{1/2}/\partial \text{pH} = 0$ ,  $\Delta E_{1/2} > \Delta \psi_1$ . Thus, increase in salt concentrations would shift  $E_{1/2}$  to positive potentials by a value higher than that of the  $\psi_1$ -potential variation. This is actually observed in experiments. An example may be given by the considerable shift of  $E_{1/2}$  (with increase in ionic strength) of second ketone waves in an alkaline medium, where the particles discharged are anions<sup>62</sup>.

When concentrations of indifferent electrolytes are insufficient, especially if they do not involve polyvalent or surface-active cations, many organic anions will be polarographically inactive, or their waves will be masked by the discharge current of the supporting electrolyte<sup>80-83</sup>.

The double layer structure will also exert an appreciable effect on kinetic waves involving anions. For instance, the addition of cations of tetraethylammonium will increase even the "space" kinetic wave of discharge of maleic acid monoanions<sup>30</sup>. The cation effect is still greater with "surface" kinetic waves. The addition of cations greatly increases the concentration of anions in the reacting layer and, thus, the height of the kinetic wave<sup>8,30,79,82</sup>. An especially marked effect is exerted by surface-active

cations. Thus VOLKOVÁ showed that in the adsorption of cations during the drop time (in accordance with  $i-t$  curves) the density of the kinetic current of recombination of weak acid anions will also be increased<sup>79,82</sup>.

The dependence of  $E_{1/2}$  and the kinetic to diffusion current ratio  $i_i/i_d$  on the ionic strength (in a 1:1-charged electrolyte) for a "space" kinetic wave of discharge of maleic acid monoanions is shown in Fig. 4. Though the wave is of a "space" type<sup>30</sup>,

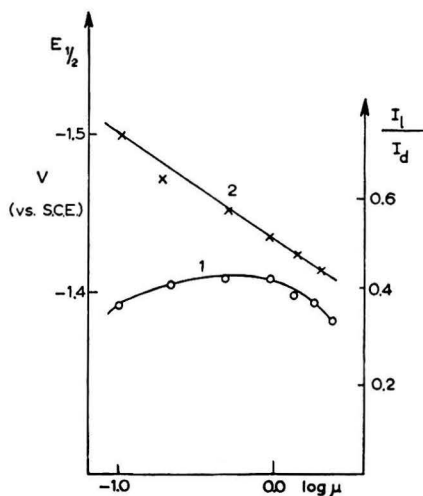


Fig. 4. The limiting to diffusion current ratio (1) and  $E_{1/2}$  (2) of the third maleic acid (0.455 mM) wave in a borate solution of pH = 8.00, as functions of the ionic strength.

its  $E_{1/2}$  will still be affected, to a certain extent, by variation of pH in the electrode-surrounding layer. This may be seen from the relatively small shift in  $E_{1/2}$  with increase in the ionic strength ( $\Delta E_{1/2}/\Delta \log \mu \approx 65$  mV); apparently this is, to some extent, (with an additional coefficient below unity) accounted for by the second term in eqn. 6. The effect of  $(\text{pH})_s$  variation is apparently due to the relatively small thickness of the reaction layer, where the interaction of maleic acid dianions and proton donors takes place.

It follows from Fig. 4 that variation of  $i_i/i_d$  with ionic strength is unimportant. For processes proceeding only in the bulk of the solution and at a sufficient thickness of the reaction layer, the ionic strength should have no effect on the kinetic current, with the exception of the insignificant salt effects (on dissociation constants and protonation rate constants). In the case considered of a "space" current and a not too thick reaction layer, there will be the effect of the ionic strength; however, the increase in anion concentration in the reaction layer with increasing ionic strength, is apparently almost compensated by a higher pH in the electrode-surrounding layer (Fig. 4).

#### ESTABLISHMENT OF RELATION BETWEEN THE STRUCTURE OF ORGANIC SUBSTANCES AND $E_{1/2}$ OF THEIR REDUCTION WAVES

The above data show that not only pH and the ionic strength of the medium, but also the nature and concentration of buffer components and indifferent electrolytes<sup>27,61</sup>

should be taken into account in determining  $E_{1/2}$  of irreversible polarographic waves for the purpose of comparing them with structures of organic compounds of certain series, or with the nature of substituents in these compounds.

An important effect on  $E_{1/2}$  will be exerted also by the charge of the particle undergoing discharge. Thus, in discharge of cations of isomeric pyridine aldehydes<sup>84</sup> and of *p*-iodoaniline<sup>85</sup> the  $E_{1/2}$  values observed appear to be more positive by  $\sim 300$  mV, while discharge of *p*-iodophenolate anion occurs at potentials  $\sim 300$  mV different from those predicted from the theory without correction for the double layer effect<sup>84,85</sup>.

It will be noted that besides the factors mentioned,  $E_{1/2}$ , even of reversible waves, may be affected also by kinetics of electrode-adjacent reactions, in particular by dimerization of electrode products. In the reduction of benzaldehyde and acetophenone, for instance, the products of a reversible electrode reaction are dimerized<sup>64</sup> and, consequently,  $E_{1/2}$  of their first waves becomes more positive with increase in the depolarizer concentration, as is consistent with theory<sup>86</sup>. It will be of interest to note that, as shown by polarograms of the above compounds corresponding to further reduction of free radicals formed in the first step,  $E_{1/2}$  of second waves becomes more negative with increase in the depolarizer concentration, so that the first and second waves are drawn apart on polarograms. The shift in  $E_{1/2}$  of the second wave may be explained by allowing for the fact that the path of the reaction involving free radicals depends on the ratio of the rates of two competing reactions<sup>25,26</sup>, *i.e.* on further reduction of radicals (resulting in the second wave) and their dimerization to non-reducible pinacol. The increase in the dimerization rate with the depolarizer concentration is faster than that of the electrode process, and to obtain the second wave it is necessary to raise the rate of electrochemical reduction of the radicals, *i.e.* of the cathode potential of the electrode.

Sometimes the shift of  $E_{1/2}$  with increased depolarizer concentration is caused by variation of the  $\psi_1$ -potential due to adsorption of the electrode products of an ionic (or dipole) nature<sup>61</sup>. This is observed, for example, in the reduction of certain nitro-compounds<sup>61,87-89</sup> yielding corresponding hydroxylamine derivatives in an acid medium.

#### SUMMARY

1. The effect of the double layer structure on the kinetics of electrode processes is due, in the general case, to three factors:

(a) variation of the effective potential difference between the electrode and the particle under discharge;

(b) variation of ion concentrations (in particular for hydrogen ions) in the layer surrounding the electrode, as compared to the bulk of the solution;

(c) variation of sorbtivity, which is especially important for processes preceded by a chemical reaction.

The effect of these factors on polarographic waves of different natures is shown.

2. Reduction waves of organic substances consuming protons in the potential-determining step represent processes preceded by fast protonation. It is shown that in the majority of cases protonation preceding electron transfer takes place on the electrode surface and involves adsorbed particles, *i.e.* it occurs under conditions of maximum effect on the double layer structure and on factors accounting for the adsorption on the electrode.

3. It is shown that the rate of preceding reactions in the surface layer is considerably higher than in the bulk of the solution, thus "surface" kinetic waves, for example, preceded by protonation may be observed even at pH's higher by 7-8 units than the  $pK_A$  value of the acid under discharge.

4. It is shown that in comparing the  $E_{1/2}$ 's of irreversible waves of organic compounds, not only pH, but also the ionic strength, buffer capacity and the nature of buffer and indifferent electrolyte components, as well as the possible effect on  $E_{1/2}$  of the electrode products formed, are to be taken into account when determining the  $E_{1/2}$  value.

5. Investigation of the effect of ionic strength on polarographic waves often allows the nature of the particle under discharge and the mechanism of the electrode process to be judged.

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## Short Communications

### Studies on formal potentials of the Tl(III)–Tl(I) system and potentiometric determination of thallium(III) by reduction with titanium(III) and vanadium(II)\*

Thallium(III) is easily reduced to a monovalent state with stannous, titanous, vanadous and chromous solutions, but direct titrimetric procedures using these reductants have not so far been attempted for determination of thallium. It seems that air-sensitivity and the unstable nature of the reductants have restricted their use for occasional single determinations, but recently certain methods<sup>1</sup> have been devised for storage of air-sensitive solutions and such equipment has been made available commercially. It is also claimed that if pure reagents are used and if solutions are stored properly, their strengths can be kept unchanged indefinitely. The use of strong reductants in titrimetric analysis eliminates the prior reduction of the substance to be analysed from the higher to the lower valency state, with reducing agents or reductor columns.

Among the methods so far used for titrimetric determination of thallium, only the iodometric<sup>2</sup> method applies for thallium(III). In the present investigation an attempt has been made to develop titrimetric methods for determination of thallium(III) by reduction with titanium(III) and vanadium(II) solutions. Earlier, some methods for reductometric determination of thallium(III) with chromium(II)<sup>3</sup> and ascorbic acid<sup>4</sup> have been reported from these laboratories, but the reduction with titanium(III) or vanadium(II) was found to be somewhat slow at room temperature, and it was decided that the formal potentials of the Tl(III)–Tl(I) system in different acids and at different acid concentrations should be studied, to find optimum conditions for the smooth reduction of thallium(III). No attempt has been made in the present investigation to use visual indicators and potentiometric end-point determination has always been applied.

#### EXPERIMENTAL

##### *Determination of formal potentials of the Tl(III)–Tl(I) system in different acids*

Thallic chloride, sulphate and nitrate solutions were prepared by dissolving the respective pure salts in water, while thallic perchlorate was prepared by dissolving the metal in a known excess of perchloric acid. The exact strengths of these solutions were determined iodometrically<sup>2</sup> after oxidation with bromine. Thallium(III) solutions were prepared by dissolving freshly precipitated hydrated thallic oxide in the respective acids. Solutions were then prepared containing Tl(III)–Tl(I) in the ratio 1 : 1, and the final acid concentrations were varied from 1–5 *F* (except in the case of hydrochloric acid).

The cell used for formal potential measurements consisted of a bright platinum electrode dipping into the solution containing Tl(III)–Tl(I) ions at a known acid con-

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centration. A S.C.E. was used as comparison electrode and it was connected through a salt bridge, consisting of agar-agar saturated with the potassium salt of the particular acid, *i.e.*, potassium chloride, sulphate, nitrate and perchlorate. The E.M.F. measurements were carried out using a Doran pH meter (Universal Model No. 4981) and readings were converted to the hydrogen scale. Table I gives the results of formal potentials of the Tl(III)-Tl(I) system in different acids and the effect of acid concentration.

TABLE I  
FORMAL POTENTIALS OF THE COUPLE Tl(III)-Tl(I)

Acid concentration (F)	Formal potentials vs. hydrogen electrode $E_f(V)$			
	HCl	H <sub>2</sub> SO <sub>4</sub>	HNO <sub>3</sub>	HClO <sub>4</sub>
0.5	0.77	1.22	1.23	1.25
1.0	0.77	1.22	1.23	1.26
1.5	—	1.22	1.23	1.26
2.0	—	1.22	1.23	1.27
3.0	—	1.22	1.23	1.27
4.0	—	1.21	1.23	1.28
5.0	—	1.21	1.22	1.28

It has been observed that, except in the case of perchloric acid, the formal potential of the couple is independent of concentration of the acid, indicating the formation of chloro-thallate, sulphato-thallate and nitrate-thallate complexes. The low value of the formal potential in hydrochloric acid indicates strong complexing, even at low acid concentration. With perchloric acid, either no complexing takes place, or it is incomplete. There is also an indication that the oxidising properties of thallium(III) in different acids should be in the order: HClO<sub>4</sub> > HNO<sub>3</sub> > H<sub>2</sub>SO<sub>4</sub> > HCl.

#### Potentiometric titration of thallium(III) with titanium(III)

Preparation and standardisation of titanous chloride and sulphate solutions were according to the method of KNECHT AND HIBBERT<sup>5</sup> and the solution was stored in an automatic burette<sup>1</sup> used for storing air sensitive reagents. Thallium(III) solutions used were the same as had been used for measuring formal potentials. The titration vessel and the procedure for carrying out the titration have been described earlier<sup>3</sup>. The equivalence point was indicated by a sudden drop in the potential. The results of some of the determinations are given in Table II.

TABLE II

Medium	$\frac{\Delta mV}{\Delta ml}$	Amount of thallium (in mg)		Error %
		Taken	Found	
N HCl	1800	25.7	25.25	-1.4
2 N HCl	2100	51.8	51.38	-0.8
2 N H <sub>2</sub> SO <sub>4</sub>	2400	75.8	75.44	-0.5
2 N H <sub>2</sub> SO <sub>4</sub>	2250	45.8	45.90	0.2
2 N HClO <sub>4</sub>	2650	63.4	63.85	0.7
3 N HClO <sub>4</sub>	2700	80.0	80.32	0.4

The titrations of thallium(III) chloride in 2–3 *N* HCl were performed at 60–80° while those of thallium(III) sulphate in 2–3 *N* H<sub>2</sub>SO<sub>4</sub> were performed at 30–40° and proceeded smoothly. The titration could also be performed in the presence of perchloric acid, which is not reduced<sup>6</sup> under the conditions used, but in the case of nitric acid, more titrant is used, indicating reduction of nitrate ions.

*Potentiometric titration involving a vanadium(II) reductant*

The preparation and standardisation of vanadous solutions were carried out as described by VOGEL<sup>7</sup>. The titration procedure was the same as that used in the case of titanium(III) and the results of various determinations and the effect of different acids are given in Table III.

TABLE III

Medium	$\frac{\Delta mV}{\Delta ml}$	Amount of thallium (in mg)		Error %
		Taken	Found	
N HCl	2250	25.0	14.8	—0.8
2 N HCl	2400	50.2	49.82	—0.8
2 N H <sub>2</sub> SO <sub>4</sub>	2750	25.0	25.10	0.4
2 N H <sub>2</sub> SO <sub>4</sub>	2600	15.6	15.71	0.7

The reduction of thallium(III) by vanadium(II) proceeds more smoothly, compared with the reduction by titanium(III), and also the reduction takes place more easily in sulphuric acid than in hydrochloric acid. For both reductants, a method employing excess reductant can also be followed; excess reductant is then determined by back titration with iron(III) solution.

## SUMMARY

The effects of different acids and their concentrations on the formal potentials of the Tl(III)–Tl(I) couple have been studied, with the object of finding optimum condition for reduction of thallium(III). Potentiometric determination of thallium(III) by reduction with titanium(III) and vanadium(II) have been described and it was observed that the reduction is more smooth in sulphuric than in hydrochloric acid media.

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## A new parameter $i_p/i_d$ in oscillographic polarography

### INTRODUCTION

The determination of the number of electrons involved in a reduction is important in any fundamental study of polarography. It is, however, probably true to say that there is considerable uncertainty about the number of electrons involved in many electrode processes. Examples of this are available from many different sources<sup>1</sup>. The most probable reason for this uncertainty is connected with the diffusion coefficient, which of all the quantities involved in the Ilkovič equation, is the most difficult to determine accurately<sup>2</sup>. It is to be expected, therefore, that any method which permits the determination of  $n$  (the number of electrons involved in the electrode process) and eliminates the necessity of knowing  $D$  (the diffusion coefficient) will be a welcome advance in polarography.

In the present work, a study of reduction waves suggested the basis of a method for the determination of  $n$  without the necessity of knowing  $D$ . The value of  $n$  is determined simply. The reasoning which led to the development of the new parameter is outlined below.

### THEORY

#### *Comparison of two oscillographic reduction waves*

If a solution is polarographed at a potential more negative than the reduction potential of the electroactive constituent, then continuous reduction will take place all the time and a wave similar to that shown in Fig. 1 is obtained. Part A corresponds

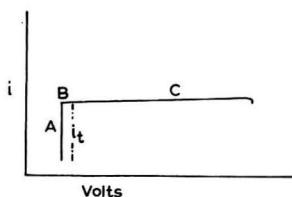


Fig. 1.

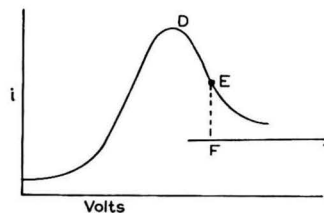


Fig. 2.

to the five-second delay period, when the voltage is steady. The current rises because the drop is growing during reduction. At the point B, the changing potential is applied during the last few seconds of the life of the mercury drop. There is almost no increase in current during this time because the increase in surface area of the drop is very small. The equation representing the flat portion of the curve is given by

$$i_t = 706nD^{1/2}Cm^{3/2}i^{1/2}$$

This is so because the cathode ray tube is a fast response instrument. The continuous reduction wave may be compared with the normal oscillographic reduction wave

(Fig. 2). The points on the peak are not "equilibrium points", *i.e.*, if one could take the situation represented by point E and "freeze" it, the current reading would fall until it reached the point F on the continuous reduction wave. The equation for the peak height is

$$i_p = 1.25 \cdot 10^6 D^{\frac{1}{2}} m_1^{\frac{1}{2}} n^{\frac{1}{2}} C$$

where  $i$  is measured in  $\mu\text{A}$ . The symbols have their usual significance except  $m_1$ , which is the drop mass in mg. The relation between the two is  $m_1 = m t_1$ , where  $t_1$  is the drop time during the measurement of  $i_p$  etc.

From a comparison of the equations for these two waves, it will be observed that the outstanding difference is connected with  $n$ , *i.e.*,  $i_t \propto n$  and  $i_p \propto n^{\frac{1}{2}}$ . Since  $n$  is involved to a different degree in the two equations, it might be expected that a comparison would yield a third equation, enabling  $n$  to be calculated. If  $i_p$  is divided by  $i_t$  the following equation results:

$$\frac{i_p}{i_t} = \frac{k n^{\frac{1}{2}} t_1^{\frac{1}{2}}}{t^{\frac{1}{2}}}$$

where  $k$  is a constant. The time  $t$  at which  $i_t$  is measured is five sec. Under these conditions,  $i_t$  is replaced by the symbol  $i_a$ . The drop time  $t_1$  for the measurement of  $i_p$  is 6.8 sec. The choice of these values is dictated by experimental convenience. The above equation reduces to the following form:

$$\frac{i_p}{i_a} = K n^{\frac{1}{2}}$$

If  $i_p/i_a$  is plotted against  $n^{\frac{1}{2}}$  for various reductions, then according to this equation, a straight line should be obtained. If this is the case, then by measuring  $i_p/i_a$  for a reduction,  $n$  can be calculated. The only condition which must be fulfilled is that the separate equations for  $i_p$  and  $i_a$  must hold, *i.e.*, the reductions must be reversible. This relationship was tested experimentally.

#### EXPERIMENTAL

In the literature<sup>2,3</sup> the following reversible reductions have been well established.

- (a) trioxalato ferric iron,  $\text{Fe}(\text{C}_2\text{O}_4)_3^{3+}$ , (1 electron reduction);
- (b) stannous tin,  $\text{Sn}^{2+}$ , and lead,  $\text{Pb}^{2+}$ , in chloride electrolytes, (2 electron reductions);
- (c) bismuth,  $\text{Bi}^{3+}$  in chloride electrolyte, (3 electron reduction).

A solution of each of these substances, approximately  $10^{-3} M$  with respect to the metal ion and  $1 M$  in the basic electrolyte, oxalate or chloride, was prepared. Each solution was then polarographed in the Southern Instrument Cathode Ray Polarograph K 1,000 and the peak height  $i_p$  recorded.

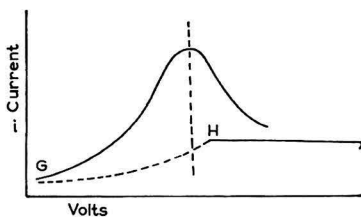


Fig. 3.

The procedure for the evaluation of  $i_a$  was more complicated. The starting potential (see Fig. 3) was moved from G to H, a position more negative than the peak value, thus ensuring continuous reduction. The current was measured at H, which was the most convenient position, *i.e.*, after the drop was five seconds old. As the starting potential was moved to a more negative value, the drop time became shorter. During measurement of  $i_p$  the longest possible drop time was chosen (*i.e.* 6.8 sec) so that the subsequent reduction in time would not destroy synchronisation. Once synchronisation had been achieved, the time required to take both measurements was about 0.5 min.

## RESULTS

The following results were obtained:

TABLE I

Number of electrons transferred	Metal ion	Basic electrolyte	$i_p/i_a$
1	Fe <sup>3+</sup>	oxalate	3.44
2	Sn <sup>2+</sup>	chloride	3.84
2	Pb <sup>2+</sup>	chloride	3.87
3	Bi <sup>3+</sup>	chloride	4.18

The plot of  $i_p/i_a$  against  $n^{1/2}$  is a straight line, as can be seen from Fig. 4.

A number of 'unknown' solutions were polarographed and  $i_p/i_a$  recorded. Using the

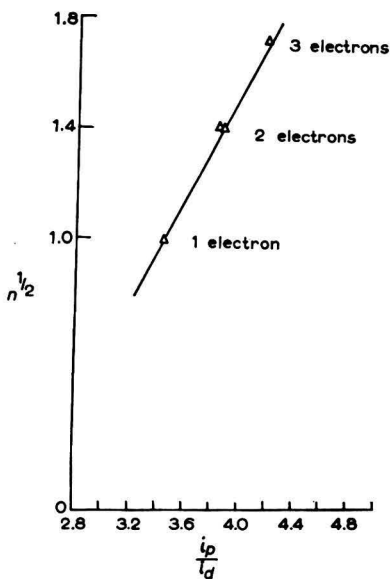


Fig. 4.

plot, the number of electrons involved in the reductions was calculated. Results were correct in every case, except where the reduction was very irreversible.

In this connection, the case of nickel(II) was investigated. The polarography was first carried out in 1925<sup>4</sup> yet, to-day, there is still disagreement between the results of investigators. CAGLIOTI<sup>5</sup> and co-workers claim that the reduction involves one electron reduction to Ni(I), while HUME AND KOLTHOFF<sup>1</sup> support the view that the reduction is to the metal. In the present work it was found that the reduction of Ni(II) in chloride electrolyte was too irreversible to use the method outlined above. However, when potassium cyanide was used to complex the nickel, a well-formed wave was obtained for Ni(II), which gave a value of 3.3 for the ratio  $i_p/i_a$ , indicating a one-electron reduction in agreement with CAGLIOTI.

#### DISCUSSION

The value of  $i_p/i_a$  for an irreversible reduction is less than for an ideal reduction. However, this approach can still be used for those reductions where divergence from reversibility is small. In such cases, increasing the temperature<sup>6</sup> will bring the value of  $i_p/i_a$  up to the theoretical value.

Although the value of  $i_p/i_a$  can be less than ideal, it cannot be greater. Therefore, if  $i_p/i_a$  falls, for example, between the theoretical values for a 2- and 3-electron reduction, it cannot be related to a 2-electron reduction. It can only be a somewhat irreversible 3-electron reduction. With time, small fluctuations in the values of  $i_p/i_a$  for a given reduction occur. To eliminate this error, the values of  $i_p/i_a$  for standard solutions were always taken at the same time as those for the unknown solution.

#### SUMMARY

A method for the determination of  $n$ , the number of electrons involved in a reduction (or oxidation), has been developed. It is simple in operation and does not require a knowledge of concentration or the diffusion coefficient  $D$  of the electro-active species.

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## The catalytic polarographic current of a metal complex. The nickel(II)-pyridine system

A *catalytic* polarographic wave is obtained when the product of the electrochemical reaction undergoes a rapid chemical reaction to reform the initial starting material. Several types of catalytic mechanism have been described in the literature<sup>1</sup>. However, no example of a catalytic mechanism involving a metal complex has yet been reported.

We have found recently that solutions of  $\text{Ni}^{2+}$  containing a small quantity of pyridine exhibit a small prewave (before the main wave of the  $\text{Ni}(\text{H}_2\text{O})_6^{2+}$  reduction), as shown by the dashed lines of Fig. 1. The height of this prewave varies with pyridine

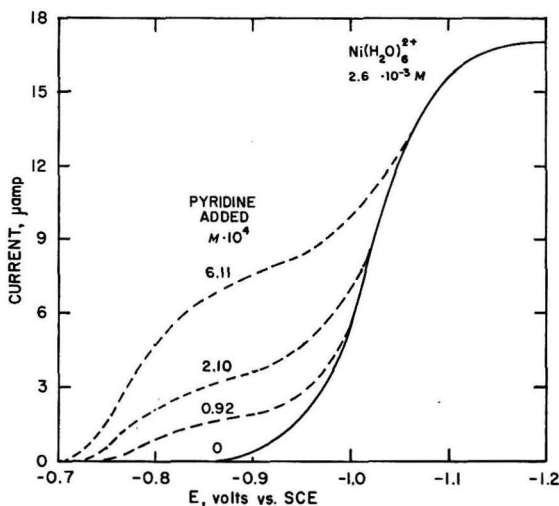
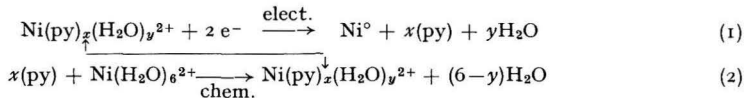
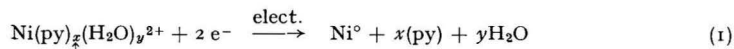


Fig. 1. Polarograms of  $\text{Ni}(\text{H}_2\text{O})_6^{2+}$  and  $\text{Ni}(\text{py})_x(\text{H}_2\text{O})_y^{2+}$  complexes. The solutions contained  $2.60 \cdot 10^{-3} M \text{ Ni}^{2+}$ ,  $3.36 \cdot 10^{-3} M \text{ Ca}^{2+}$  [as a maximum suppressor<sup>2</sup>], and  $0.10 M \text{ NaAc}$ . The  $\text{pH} = 7.10 \pm 0.05$ . ————  $[\text{py}] = 0$ , - - - - - at various pyridine concentrations.

concentration, but in a non-linear manner, as is to be expected for a catalytic process<sup>3,4</sup>. Furthermore, this current is several times larger than the diffusion current to be expected, had the pyridine been completely bound to  $\text{Ni}^{2+}$  as a 1:1 complex. Actually, the percentage association is less than 100% under these solution conditions, and, hence, the true enhancement is even greater. The height of the prewave, for a constant pyridine concentration, is also dependent on the concentration of the  $\text{Ni}^{2+}$  ion. These concentration dependences are similar to those obtained for other types of catalytic waves<sup>3</sup>.

The temperature coefficient of the prewave current (approximately + 5% per °C) is greater than that expected for a diffusion limited process (+ 2% per °C)<sup>3</sup>.

Apparently, the reacting species in this case is a Ni(pyridine)<sub>x</sub>(H<sub>2</sub>O)<sub>y</sub><sup>2+</sup> complex (where *x* and *y* are unknown) which has a much lower reduction overpotential than that of Ni(H<sub>2</sub>O)<sub>6</sub><sup>2+</sup>. It is well known that the *E*<sub>1/2</sub> of the Ni<sup>2+</sup> reduction is shifted to more positive potentials, if an excess of pyridine or Cl<sup>-</sup> is present<sup>5</sup>. The reaction mechanism can be represented by a pair of reactions of the type:



This mechanism is somewhat analogous to the hydrogen catalytic current mechanism<sup>1</sup>, whereby a proton binds to an organic compound, with subsequent lowering of its overpotential, which leads to a small prewave. The organic compound, freed by the electrochemical reaction, then recombines with protons in solution to regenerate the initial species. Thus, the prewave is catalytic in nature.

Adsorption also appears to be an important step in the mechanism [as is also true in the hydrogen case<sup>1</sup>]. A detailed investigation of the mechanism of this process and its analytical applications is now in progress.

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<sup>1</sup> P. DELAHAY, *New Instrumental Methods in Electrochemistry*, Interscience Publishers, New York, 1954, pp. 87-114.

<sup>2</sup> N. V. EMERLIANOVA AND J. HEYROVSKÝ, *Trans. Faraday Soc.*, 24 (1938) 257.

<sup>3</sup> L. MEITES, *Polarographic Techniques*, Interscience Publishers, New York, 1955, pp. 78-82.

<sup>4</sup> I. M. KOLTHOFF AND J. J. LINGANE, *Polarography*, Vol. 2, 2nd edn., Interscience Publishers, New York, 1952, p. 853.

<sup>5</sup> See reference 4, page 486.

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## Book Reviews

*An Introduction to Spin-spin Splitting in High Resolution Nuclear Magnetic Resonance Spectra*, by JOHN D. ROBERTS, W. A. Benjamin, Inc., New York, 1961, 105 pages.

This small volume is a fine do-it-yourself instruction manual for the analysis of high-resolution nuclear magnetic resonance spectra of very simple molecules. It provides complete details of the method of calculation and many exercises, which provide opportunities for practice.

A serious reader may develop from this book a considerable talent for the analysis of the type of spectra discussed, and even a general understanding of some of the principles involved. However, little consideration is given to the quantum-mechanical basis for the techniques used, in spite of the dust jacket advertisement that "no prior knowledge of quantum mechanics, or the mathematics thereof, are assumed". As a result, one who seeks a genuine understanding of the underlying principles must search elsewhere.

Professor ROBERTS has written a book which can be of value to a reader with specialized interests, but it is apt to leave him in a state of mental frustration. Anxious to apply his newly-acquired skill, the reader may attempt the analysis of the spectrum of a more complex molecule, only to discover that the techniques he has learned are inadequate for virtually all cases beyond those he has already encountered as examples or exercises in the book. The powerful techniques of group theory, for example, are entirely omitted.

This book will be welcomed by those for whom it was written – students and organic chemists interested in the practice of analysis of high-resolution NMR spectra.

DONALD R. WHITMAN, Case Institute of Technology, Cleveland, Ohio

*J. Electroanal. Chem.*, 4 (1962) 191

*Dr. L. Medicus: Einleitung in die chemische Analyse. I. Band. Kurze Anleitung zur qualitativen Analyse*, by MARGOT BECKE-GOEHRING AND JOHANNES WEISS, 28th revised edn., Theodor Steinkopff Verlag, Dresden and Leipzig, 1961, 150 pages, D.M. 10.70.

Qualitative analysis of inorganic compounds is an important part of inorganic chemistry. However, in recent years, the significance of qualitative analysis in its classical form has been greatly lessened by the introduction of more rapid methods of investigation, such as spectrochemical analysis. Nevertheless, basic knowledge of the conventional classical system of qualitative analysis is still indispensable for chemists.

The first part of the book discusses informative qualitative investigations. Various flame tests, borax and phosphorus bead tests, ignition tests, and specific reactions of some cations and acids are described. Following these, determination of cations and anions in qualitative analysis is described. Finally, the sequence of qualitative analytical tests and the procedure to be followed are presented in a tabulated scheme.

At present, we can also use various other systems instead of the classical method of qualitative analysis. These methods, *e.g.* the Okač system, are not mentioned in the present work. However, semi-micro methods, which are important from a practical aspect, are briefly discussed and the procedure is shown in tables.

In the final chapter, a survey is made of the treatment of fluxes, and the behaviour of some elements, which had not been mentioned during the course of analysis treated in the book, is described from the aspect of group reactions.

The new enlarged edition of the famous *Medicus* is a valuable help for beginners studying qualitative analysis. The compact style is a characteristic of this book, which greatly facilitates a survey of the material presented.

E. PUNGOR, University of Budapest

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*Dosages Colorimétriques des Éléments Minéraux*, by G. CHARLOT, 2nd edn., Masson, Paris, 1961, 380 pages, N.F. 45.

This second edition of the well known book by G. CHARLOT has been produced because new colorimetric reagents and new colorimetric reactions are described almost every day in the literature. Writing such a book then presents problems in selecting the best reagents and methods from the astronomical quantity of material published.

Presenting a method, a reagent or a reaction etc. as a *good* one is the responsibility of the author, and the procedure should preferably have been critically tested before being adopted and recommended. In fact, the analytical methods described in the classical work of TREADWELL, from which several generations of chemists learned analytical chemistry, were all tested in the author's laboratory. But it is impossible to adopt this procedure to-day, so that, unavoidably, any book of this kind contains some incomplete points. For example, in this, otherwise very good, book by CHARLOT, no reference can be found to the reagent Xylenol orange, which has been used with very good results by many authors for different metallic ions, and also by the reviewer for the determination of traces of iron. But this consideration does not diminish the merits of CHARLOT's book; it is only a statement of the difficulties encountered by every author writing such books.

This book is divided in two principal parts: the first one (138 pages) deals with the theoretical principles of colorimetric and spectrophotometric analysis, and gives a description of the methods for separation of trace elements by different techniques. The second part (230 pages) is devoted to the analysis of 64 elements and to a brief discussion of the rare earth elements. Such a wealth of material is assembled, that, occasionally, unavoidably brief descriptions of the method are given. Reference to the original literature is then necessary; these references are very carefully given.

This book can be strongly recommended, particularly as a very good source of information.

G. MILAZZO, Istituto Superiore di Sanità, Rome

*J. Electroanal. Chem.*, 4 (1962) 192

*Einführung in die Theorie der quantitativen Analyse*, by MARGOT BECKE-GOEHRING AND EKKEHARD FLUCK, Theodor Steinkopff Verlag, Dresden and Leipzig, 1961, 151 pages, D.M. 13.60.

In the last decades, analytical chemistry has developed to a remarkable extent. Conventional reactions have been increasingly supported by sound theoretical knowledge of the principles of reactions used for analytical purposes. Because of these changes, a great number of scientists now regard analytical chemistry as applied physical chemistry. Thus, anyone who intends to study analytical chemistry must also deal with the theory on which chemical analysis is built up. Theoretical fundamentals of classical and instrumental analytical techniques have many ramifications. Thus, the authors of this book faced a very difficult problem when selecting material for their book.

In a very commendable way, this book, written mainly for beginners, discusses the reactions which are fundamental to conventional, classical analysis. Thus, problems occurring in the field of acid-base reactions, definition of pH values, buffers and problems of solubility (which are of great importance in precipitation titrations), theoretical fundamentals of complexometric titrations, redox reactions, redox potentials, and methods of end-point indication are briefly surveyed by the authors. Finally, a short summary of electrogravimetry is presented, and some methods are described which can be used with great success in gas analysis.

Considering that the book is written mainly for beginners, the chapter on acid-base reactions is of particularly great value. The use of diagrams to illustrate  $\text{pH}/\log c$  relationships greatly facilitates the understanding of reactions of weak acids and bases. The examples explained in the book will be a considerable help to chemists beginning to study and to analysts, for acquiring a sound knowledge of some theoretical problems of chemical analysis. The tabulated summary facilitates the calculation of pH values in solutions of various acids and salts.

E. PUNGOR, University of Budapest

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## 1. Fundamental electrochemistry

**457 – Oxidation-reduction mechanisms** (in English). F. R. Duke (Institute for Atomic Research, Iowa State University, Ames, Iowa, U.S.A.). *J. Chem. Educ.*, 38 (1961) 161–163. The process of electron transfer taking place during oxidation–reduction reactions is considered. In reactions involving a cation and an anion, the intramolecular electron transfer is provided by the bond. When two cations are involved, the transfer may be accomplished by a basic bridge. Many reactions where anions alone are involved permit the transfer through an intermediate formed between the anions. In the case of complex ions containing unsaturated and conjugate systems, the electron transfer takes place directly from one particle to another by a process similar to tunnelling. [D.S.Ru.]

**458 – Theory of stationary electrode polarography** (in English). W. H. Reinmuth (Department of Chemistry, Columbia University, N. Y., U.S.A.). *Anal. Chem.*, 33 (1961) 1793–1794. The author reports the derivation of explicit solutions, in the form of infinite series, concerning the theory of voltammetry with linearly changing electric tension at stationary planar and spherical electrodes, under conditions of Nernstian or slow charge transfer. Irreversible first-order chemical decomposition following Nernstian charge transfer is also considered. A log plot criterion of reversibility, applicable to planar electrodes and approximately obeyed at spherical electrodes, is proposed. [Su.Mo.Ce.]

**459 – The cell  $\text{Hg}/\text{Hg}_2\text{Cl}_2(\text{s}), \text{HCl}/\text{Pt}-\text{H}_2$  (1 atm.) in organic solvents and their mixtures with water. IV.  $\text{Hg}/\text{Hg}_2\text{Cl}_2(\text{s}), \text{H}_2\text{O}$  (100-x), Äthanol (x),  $\text{HCl M}/\text{H}_2$  (1 atm.), Pt** (in German). K. Schwabe und M. Kunz (Institut für Elektrochemie und physikalische Chemie der Technischen Hochschule, Dresden, Deutschland). *Z. Elektrochem.*, 64 (1960) 1188–1190. Nachdem die Autoren in vorangegangenen Arbeiten Spannungsmessungen an der Kette  $\text{Hg}/\text{Hg}_2\text{Cl}_2(\text{s}), \text{HCl}/\text{Pt}-\text{H}_2(1 \text{ atm.})$  in wässrigen Gemischen der Lösungsmittel Glykol, Dioxan und Methanol durchgeführt hatten, berichten sie über gleichartige Messungen in Wasser–Äthanolmischungen bei verschiedenen Molenbrüchen. Die Standard-Spannung wurde nach dem Extrapolationsverfahren von McInnes und Brown berechnet. Aus dieser und den Mess-Werten wurden die Aktivitätskoeffizienten und die primären und totalen Mediumeffekte ausgerechnet. Die primären Mediumeffekte werden mit den Dielektrizitätskonstanten der Lösungsmittel verglichen und festgestellt, dass sich für Äthanol bei kleinerer Dissoziationskonstante ein grösserer Wert als für Methanol ergibt. Die Aktivitätskoeffizienten waren etwas höher, die primären Mediumeffekte etwas niedriger als frühere Literatur-Werte. Infolge der Kompensation beider Abweichungen wurde beim totalen Mediumeffekt eine bessere Übereinstimmung mit den Literatur-Werten erzielt. [He.We.]

**460 – Influence of anions on the kinetics of dissolution of metals** (in Russian). Ya. M. Kolotyrkin (L. Ya. Karpov Institute of Physical Chemistry, U.S.S.R.). *Uspekhi Khim.*, 31 (1962) 322–335. A review dealing with the influence of anions on the dissolution of metals is given, based on some practical examples (e.g. cadmium in 1.0 N  $\text{H}_2\text{SO}_4 + \text{KI}$ , dissolution of an indium amalgam in a solution of 0.01 N  $\text{In}(\text{ClO}_4)_3 + 0.001 \text{ N HClO}_4$  containing varying amounts of NaBr, NaCl or NaI). Some values of solution potentials of metals in solutions containing halides are given. [Ot.So.]

**461 – Diffusion polarisation of the hydrogen electrode. II** (in English). A. H. M. Cosijn (Laboratory of Analytical Chemistry, State University, Utrecht, The Netherlands). *J. Electroanal. Chem.*, 3 (1962) 24–35. The present paper deals with the measurement of current–electric tension curves at the stationary platinised platinum–hydrogen electrode in 0.1 M KCl, 0.1 M  $\text{K}_2\text{SO}_4$ , (1:1) acetic acid–sodium acetate and (1:1) mono-dihydrogen phosphate solutions. The results agree with the theoretical predictions published in part I of the paper. [Author]

**462 – The “äussere Überführung” (external transfer) of molten  $\text{TlCl}$  and  $\text{ZnCl}_2$**  (in German). W. Fischer and A. Klemm (Max-Planck-Institut für Chemie, Mainz, Deutschland). *Z. Naturforsch.*, 16A (1961) 563–568. Die Elektroendosmose von geschmolzenem  $\text{TlCl}$  und  $\text{ZnCl}_2$  durch ein U-förmiges Diaphragma aus  $\text{Al}_2\text{O}_3$  Splittern bis zu 0.2 mm Durchmesser wurde zwischen  $\theta = 435^\circ$  ( $325^\circ$ ) bis  $670^\circ$  mit der Steig-

höhenmethode gemessen. Für die Überföhrungszahl des Kations gilt:  $TiCl_4$   $t^+ = 0.410 + 2.282 \cdot 10^{-4}$ , ( $\theta$  ist  $430^\circ$ );  $ZnCl_4$   $t^+ = 0.716 - 3.07 \cdot 10^{-4}$ , ( $\theta$  ist  $318^\circ$ ). [He.Be.]

**463 - Study of the anodic formation and cathodic reduction of the oxygen layer on smooth platinum electrodes** (in German). W. Böld and M. Bretter (Physikalisch-Chemisches und Elektrochemisches Institut der Technischen Hochschule, München, Bundesrepublik Deutschland). *Electrochim. Acta*, 5 (1961) 145-160.

The authors have studied the anodic formation and cathodic reduction of the oxygen layer on smooth platinum in different solutions and at different temperatures by measuring the current-electric tension curves which are obtained when a periodic triangular voltage is applied potentiostatically to the test electrode. The partial cathodic currents are negligible between +1.0 V and 1.5 V ( $E_H$ ), relative to the partial anodic currents of the two discharge reactions on which the interpretation is based; this follows from the dependence of the anodic  $i-E$  curves upon the rate of variation of voltage, and the  $H^+$  ion concentration. The currents of consecutive discharge steps during the oxidation are equal, and lead to the formation of a chemisorbed layer, Pt-O. That the anodic current is independent of the electric tension between +1.0 V and 1.5 V is explained with the aid of Temkin's kinetic expressions. The cathodic  $i-E$  curves differ greatly from the anodic, because the system of differential equations which describes the processes simplifies the case considerably for the oxidation but not for the reduction. The anodic and cathodic processes can be interpreted satisfactorily on kinetic concepts. [Fr.Cla.]

**464 - Electrometric titration of molybdic acid** (in English). S. P. Moulik (Chemical Department, University College of Science, Calcutta, India). *Sci. and Culture (Calcutta)*, 27 (1961) 45-46.

Pure molybdic acid was prepared by passing 0.1 M Na molybdate through a column of strongly acidic resin. The solution obtained has a pH of 2.26. Electrometric titration with NaOH, using a glass electrode was carried out. The titration curve has two inflexion points. The results are discussed in connection with data found in the literature. [Gio.Ser.]

**465 - Quantitative treatment of substituent effects in polarography. II. Free energy relationships in monocyclic and heterocyclic series** (in English). P. Zuman (Polarographic Institute, Czechoslovak Academy of Sciences, Prague, Czechoslovakia). *Collection Czechoslov. Chem. Commun.*, 27 (1962) 630-647.

Linear free energy relationships are devised to correlate the shifts of the half-wave electric tensions of monocyclic and heterocyclic compounds with structural changes. The compounds are divided into two classes according to reduction occurring (a) in the heterocyclic ring, or (b) in the side chain. For compounds with a reducible heterocyclic ring, substitution directly on that ring, or on a phenyl group attached to this ring, is considered. The reduction in the side chain may be influenced by substituents on the heterocyclic ring, by the kind of hetero atom and the size of the ring, and finally by substitution in the side chain. The scanty experimental data available (only 100 half-wave electric tensions) impose limitations on this treatment. [Ot.So.]

**466 - Quantitative treatment of substituent effects in polarography. III. Substituents in the ortho-position** (in English). P. Zuman (Polarographic Institute, Czechoslovak Academy of Sciences, Prague, Czechoslovakia). *Collection Czechoslov. Chem. Commun.*, 27 (1962) 648-666.

The correlation of the shifts of half-wave electric tensions of *ortho*-substituted compounds is first attempted by a linear free energy treatment. Secondly, a procedure is suggested which is based on measurements of polarographic half-wave electric tensions alone. Thirdly, from the difference of half-wave electric tensions of the *o*- and *p*-substituted compound the "polarographic *ortho*-shift" is defined, and some examples of positive and negative *ortho*-shifts are discussed. It is shown that by using *ortho*-shifts the role in steric hindrance of coplanarity can be distinguished, as well as that of hydrogen bonding. [Ot.So.]

**467 - Acetic anhydride as a non-aqueous ionising solvent. I. Conductivity and strength of electrolytes in acetic acid-free acetic anhydride** (in German). G. Jander und H. Surawski (Anorganisch-Chemisches Institut der Technischen Universität, Berlin, Deutschland). *Z. Elektrochem.*, 65 (1961) 384-394.

Zuerst wird eine Zusammenstellung der physikalischen Konstanten aus der Literatur und aus eigenen Messungen der Autoren und eine Beschreibung der allgemeinen Eigenschaften von essigsäurefreiem Essigsäureanhydrid gegeben. Als Eigenleitfähigkeit wird als optimaler Wert  $\kappa_0 = 2.3 \cdot 10^{-8} \text{ Ohm}^{-1} \text{ cm}^{-1}$  angegeben. Eine weitere Tabelle gibt den Grad der Löslichkeit verschiedener anorganischer und organischer Stoffe in Essigsäureanhydrid an. Die Autoren führten Präzisions-

Leitfähigkeitsmessungen von Salzen sowie Säuren- und Basenanalogen in diesem Lösungsmittel bei 20° durch. Als Säureanalogue wurden Acetylbromid, -chlorid und -perchlorat verwendet, als Basenanalogue Natrium-, Kalium-, Caesium- und Thallium-azetat. Bei Konzentrationen  $< 10^{-4} M$  ist für einige Salze ( $KClO_4$ ,  $KBr$ ,  $[(C_2H_5)_4N]Br$ ) die Debye-Hückel-Onsager Gleichung gültig. Die Grenzleitfähigkeiten  $\Lambda_0$ , die Dissoziationsgrade  $\alpha$  und die thermodynamischen Dissoziationskonstanten  $K_0$  der untersuchten Verbindungen konnten nach Shedlovsky berechnet werden. Mit Hilfe der Walden'schen Regel wurden Ionenbeweglichkeiten abgeschätzt und festgestellt, dass die Acetyl- und Azetationen des Lösungsmittels keinem besonderen Wanderungsmechanismus folgen. [He.We.]

(See also abstracts no. 540.)

**468 – Dipole moments and electron acceptor properties of cyclopentadienyl-metal bonds and benzenetricarbonyl chromium** (in German). (Institut für physikalische Chemie der Universität, Würzburg, Deutschland). *Z. Electrochem.*, 64 (1960) 945–951.

Die Dipolmomente von Cyclopentadienylmetallverbindungen und ähnlichen Stoffen wurden in Heptan, Benzol und Dioxan gemessen. Die Ergebnisse wurden nach der Methode von Hedestrand ausgewertet. In Cyclohexan haben axialsymmetrische Cyclopentadienyl-Metallverbindungen mit Doppelkegelstruktur stets das Dipolmoment  $\mu = 0$ . Das Dipolmoment ist auch in Dioxan Null, wenn eine reine kovalente Bindung vorliegt, wie bei den Durchdringungskomplexen  $Fe(C_5H_5)_2$  und  $Ni(C_5H_5)_2$ . Je stärker die Metall-Ring-Bindung ionogen ist, desto höher liegt das Dipolmoment der Verbindungen in Dioxan gegenüber dem in Heptan bzw. Cyclohexan und Benzol. Die Autoren führen diesen Effekt auf eine Donator-Akzeptor-Wechselwirkung zurück. Dioxan wirkt als starker Donator, die Zentralatome der Metallverbindungen bei  $Cr(C_5H_5)_2$  und  $V(C_5H_5)_2$  als schwache, bei  $Zn(C_5H_5)(C_2H_5)$  und  $Zn(C_5H_5)(C_6H_5)$  als starke Elektronenakzeptoren. Dies wird dadurch erhärtet, dass in diesen Fällen auch isolierbare Koordinations-Verbindungen mit Ammoniak bekannt sind. Bei Verbindungen mit "Sandwich-Struktur" wie  $Sn(C_5H_5)_2$  (kovalent),  $Pb(C_5H_5)_2$  (schwach polar) und  $Mn(C_5H_5)_2$  (ionogen) zeigte sich der gleiche Effekt, aber das Dipolmoment hat bereits in Heptan einen endlichen Wert (0.9–1.3 D). Im  $C_6H_6Cr(CO)_3$  wirkt der stark positivierete Benzolring als potentieller Elektronenakzeptor, das Dipolmoment ist in Dioxan schwach erhöht. Bei  $C_5H_5Mn(CO)_3$  und  $C_6H_7Mn(CO)_3$  ist der Effekt nur gering, da der Cyclopentadienylring infolge der höheren  $\pi$ -Elektronendichte nur sehr schwach als Akzeptor wirkt. Bei  $Be(C_5H_5)_2$  liegen andere Bindungsverhältnisse vor, da es schon in Heptan ein Moment  $\mu = 2.26$  D hat (in Dioxan  $\mu = 2.60$  D).  $Si(C_5H_5)(CH_3)_3$  hat in Heptan und in Dioxan das Moment  $\mu = 0.4$  D. [He.We.]

**469 – Redox electric tensions of *p*-hydroxyphenylglycine** (in Russian). Ya. M. Veprik and G. P. Faerman (Cinema Engineers Institute, Leningrad, U.S.S.R.). *Zhur. Fiz. Khim.*, 36 (1962) 502–507.

The redox electric tensions of *p*-hydroxyphenylglycine have been determined over the pH range 1–10. The oxidation of this compound was observed to take place in two stages, for each of which the normal redox electric tension was determined. The results are used to explain the change in relative reduction rates of  $AgNO_3$  by *p*-hydroxyphenylglycine and metal with varying pH of the medium. The normal redox electric tensions mentioned are tabulated for the pH range 1.04–9.98. [Ot.So.]

See also abstracts nos. 511, 533, 547, 552.

## 2. Apparatus and accessories

**470 – Arrangement for measuring electric tensions of polarizable electrodes by direct and commutator methods** (in Russian). G. M. Vainshtain (Research Institute of the Nitrogen Industry, Litishansk, U.S.S.R.). *Zhur. Fiz. Khim.*, 36 (1962) 645–647.

A simple arrangement was designed for measuring electric tensions of electrodes in the process of electrolysis by direct and by commutator methods. A special key is employed, permitting electric

tension measurements to be made using polarization current circuits which are closed or open at the moment of measurement. The electric tensions measured by the commutator method are often independent of current density changes, and are characteristic of the electrochemical process taking place at the electrode. [Ot. So.]

**471 – Modern apparatus for electrophoresis and chromatography in biochemical research laboratories** (in German). H. Pelzer. *Glas-Instr.-Tech.*, 4 (1960) 303–311.

A survey with thirty references to apparatus for electrophoresis and chromatography.

[Ca. Cas.]

**472 – Continuous electrophoresis fractionation stabilized by electromagnetic rotation** (in English). A. Kolin. *Proc. Nat. Acad. Sci.*, 45 (1960) 509–523.

A detailed description of a column shaped apparatus, suitable for micro-scale operations, in which ions or charged particles migrate under the influence of an electric and a magnetic field in a free solution, stabilization against thermal motion being achieved by rotating the column. The time required for separation is of the order of a few sec, under a gradient of 100 V/cm. A device for withdrawing samples after separation is also described.

[Ca. Cas.]

**473 – A transistorized amplifier for controlled electric tension coulometers** (in English). R. C. Probst (Savannah River Laboratory, E.I. du Pont de Nemours and Co., Inc., Aiken, S.C., U.S.A.). *Anal. Chem.*, 34 (1962) 588.

The construction of a transistorized amplifier is described. A schematic wiring diagram is shown, and some working details are discussed. The output voltage is  $\pm 15$  V at 300 mA with an input voltage swing of  $\pm 100$  V at 2 mA.

[Kl.Gr.]

**474 – A constant current microcoulometric technique for dropping mercury electrodes. The determination of the number of electrons involved in polarographic reductions** (in English).

H. B. Mark, E. M. Smith and C. N. Reilley (Department of Chemistry, University of North Carolina, Chapel Hill, N.C., U.S.A.). *J. Electroanal. Chem.*, 3 (1962) 98–111.

A constant current microcoulometric method for determining the number of electrons involved in a unit of reaction at a dropping mercury electrode is described in detail. A large capacitor is connected in parallel with the microcell, and a constant current applied to the combination. The results obtained from several tests with both reversible and irreversible reductions are discussed, and the optimum conditions for accurate results with the method are presented. The principle advantage of the amperostatic method over the usual potentiostatic method is the ease with which the number of coulombs passed during the electrolysis can be calculated.

[Authors]

**475 – Apparatus for electroconductivity measurements** (in Russian). E. S. Sevastyanov, A. I. Gorbanev and Yu. M. Kessler (Institute of Electrochemistry, Academy of Sciences, U.S.S.R.). *Zhur. Fiz. Khim.*, 36 (1962) 644–645.

A simple bridge circuit is described, said to reach an accuracy of 0.03% when measuring resistances of 1,000–100,000  $\Omega$  and capacities of 0–10,000 pF.

[Ot. So.]

**476 – Integral chronoamperometry with a simple apparatus** (in English). A. L. Beilby and A. L. Budd (Department of Chemistry, Pomona College, Claremont, Calif., U.S.A.). *Anal. Chem.*, 34 (1962) 493.

A modified circuit for the use of a manual polarograph is developed for integral chronoamperometry. Any conventional polarograph can be used. The time-current calibration procedure is described, and as an example, the diffusion charges and formal potentials for the oxidation of iodide are taken. The equation for calculating the diffusion charge at a cylindrical electrode is developed. The reproducibility of the method is within 1%.

[Kl.Gr.]

**477 – A micromethod for determining pH, base-excess, CO<sub>2</sub> pressure and standard bicarbonate value in capillary blood** (in English). O. S. Andersen, K. Engel, K. Jørgensen and P. Astrup (Rigs Hospital, Copenhagen, Denmark). *Scand. J. Clin. & Lab. Invest.*, 12 (1960) 172–176.

By means of a new device (consisting of a special capillary glass electrode and of a micro-equilibration chamber) 30–50  $\mu$ l samples of blood (anaerobically withdrawn) can be submitted to one actual and two additional (at two different values of CO<sub>2</sub> pressure) pH measurements: a particular nomogram (given in another paper) then gives the partial pressure of CO<sub>2</sub>, the base-excess and the standard HCO<sub>3</sub><sup>-</sup> value. Good agreement is obtained with the corresponding value measured in arterial blood.

[Ca. Cas.]



**478 – Multi-sweep cathode ray polarograph with two streaming mercury electrodes in a differential circuit** (in Russian). E. Görlich, J. Srzednicky and Z. Kowalski (Mining Academy, Cracow, Poland). *Zhur. Fiz. Khim.*, 36 (1962) 449–454.

A cathode ray polarograph is described, in which two streaming mercury electrodes in a differential circuit were used to obtain the voltammetric curves. The electrochemical part of the arrangement includes a device for regulating the length of the immersed part of the streaming electrodes with an accuracy of  $\pm 0.05$  mm. This enables the polarograph to be used for quantitative analysis. The rate of potential change may be varied stepwise from 14–896 V/sec. Polarographic curves obtained at the higher rate of potential change exhibit peaks. The image on the oscillographic screen is stable, making a direct reading possible. [Ot.So.]

**479 – Polarographic electrolyzer with solid indicating electrode for continuous automatic control** (in Russian). Ya. I. Turyan (Research Institute of the Nitrogen Industry, Liti-shansk, U.S.S.R.). *Zavodskaya Lab.*, 28 (1962) 98–101.

The design of the electrolytic vessel includes: continuous cleaning of the electrode surface by anode-cathodic polarization, and if necessary, amalgamation or any other galvanic metalisation, use of the same electrode in the measured, reference or electrolyte solution, and facilities for cathodic accumulation of the substance determined, when present in microgram amounts. A detailed diagram and description is included in the original paper. [Ot.So.]

**480 – A tempered polarographic cell for micro volumes** (in German). G. Anders and K. Schwabe (Central Institute for Nuclear Physics, Dresden, Germany). *Z. Chem.*, 1 (1961) 223–224.

Es wird eine verbesserte temperierbare Mikrozelle ( $1-5 \cdot 10^{-2}$  M) mit ausgezogener Tropfkapillare und Bodenquecksilber nach Art derjenigen von v. Sturm (*J. Polarog. Soc.*, (1958) 28–35) beschrieben und die Reproduzierbarkeit von Cd-Stufen ( $\sim 2.5 \cdot 10^{-5}$  M) hinsichtlich des Entlüftungsvorganges (5–7 min.) gezeigt. [He.Be.]

**481 – Electronic apparatus for measuring small changes of current or tension gradients in a circuit of electrically conducting liquids** (in English). P. N. Rao, P. D. Bhatnager and A. K. Bhattacharia (Department of Chemistry, Agra College, Agra, India). *Kolloid Z.*, 164 (1959) 127.

Two kinds of electric bridge have been used, together with a tube voltmeter as sensing instrument, for measuring small changes in current intensity or in electric tension, respectively. [Red.]

**482 – A device for the automatic reproduction and removal of stationary drop electrodes** (in Russian). A. Y. Gokhstein and Y. P. Gokhstein (Institute of Electrochemistry, Academy of Sciences, U.S.S.R.). *Zhur. Fiz. Khim.*, 36 (1962) 652–655.

A needle centered by springs is lifted by an electromagnet, which receives timed pulses from a synchronising arrangement. The drop formed is automatically removed after electrolysis by means of a small rocking-beam of glass activated by an electromagnet. The electrolytic cell may be sealed hermetically; the capillary is not shaken when the apparatus is in use. Local exhaustion of the solution before formation of a new drop is eliminated. [Ot.So.]

**483 – Polarization of thin porous electrodes** (in Russian). O. S. Ksenzhek (Institute of Chemical Technology, Dnepropetrovsk, U.S.S.R.). *Zhur. Fiz. Khim.*, 36 (1962) 633–636. Electrodes are considered, whose thickness is comparable with the effective depth of penetration of the electrode process into the bulk of the electrode. Calculated data are given for an estimation of the effect obtained by using porous electrodes, and the dependence on their thickness. Limits are defined for the range in which porous electrodes may usefully be employed. [Ot.So.]

**484 – Automatic microchemical investigation of the atmosphere. I** (in German). H. Malissa and G. Wagner (Institut für analytische Chemie und Mikrochemie der Technischen Hochschule, Wien, Österreich). *Mikrochim. Acta*, (1962) 332–339.

An automatic conductometer, with a recorder, is used for measuring the carbon dioxide content of the earth's atmosphere. It is possible to differentiate between  $\text{CO}_2$  present in the gas phase and present in the particles of the aerosol. [H.L.Ki.]

**485 – Coulometric analyser for trace quantities of oxygen** (in English). F. A. Keidel (E. I. du Pont de Nemours and Co. Inc., Wilmington, Del., U.S.A.). *Ind. Eng. Chem.*, 52 (1960) 490–493.

A new instrument for measuring oxygen is described. The method is suitable for very small quantities, from  $10^{-4}$ –1% by volume in gases, and from  $10^{-6}$ % to saturation in liquids. [Gio.Ser.]

**486 – A piston-type mercury electrode made from a fluorine-containing polymer** (in Rus-

sian). B. Ya. Kaplan and P. M. Chigirev (State Research Institute of Rare Metals, U.S.S.R.). *Zavodskaya Lab.*, 28 (1962) 101-102.

An electrode is described, suitable for the stationary-drop type of polarographic analysis, with cathodic accumulation of the substance determined. A drawing is included. [Ot.So.]

**487 – Automatic titration with direct read-out of chloride concentration** (in English). E. Cotlove and H. H. Nishi (National Heart Institute, Bethesda, Md., U.S.A.). *Clin. Chem.*, 7 (1961) 285-291.

A unit is described for use with an automatic titrator. The latter has been described previously. The concentration of  $\text{Cl}^-$  can be read in mequiv./l on a digital register. The determination requires only 0.1 ml of sample. [Gio.Ser.]

**488 – New apparatus for electrochemistry in anhydrous organic solvents** (in French). I. Gillet (Laboratoire d'électrochimie organique, Université de Liège, France). *Bull. soc. chim. France*, (1962) 377-380.

L'auteur décrit une cellule d'électrolyse et un potentiostat qui permettent de faire des mesures en milieu anhydre très résistant. La cellule est d'abord décrite avec beaucoup de minutie (4 schémas). Pour obtenir des lignes de champ parallèles, et une densité de courant uniforme, les deux électrodes utilisées sont planes et parallèles; ces électrodes qui sont amovibles, sont situées aux deux extrémités de la cellule cylindrique. Pour ne pas modifier l'uniformité du champ, la jonction électrolytique entre l'électrode de comparaison et la cellule est entièrement extérieure à celle-ci; elle y débouche par une fente latérale réglable très mince (3 mm  $\times$  20 microns) située dans la paroi cylindrique, au niveau de l'électrode étudiée. La proximité de la fente et de l'électrode (environ 20 microns) rend négligeable la tension électrique que pourrait introduire le courant d'électrolyse. La cellule, construite en verre et téflon, est étanche aux gaz; l'agitation se fait par circulation du liquide.

L'auteur décrit ensuite un potentiostat électromécanique capable de fournir une tension d'électrolyse de 235 V. L'appareil est alimenté par 3 batteries de 80 V. Il peut fournir jusqu'à 1.5 A. Le temps de réponse est 0.3 sec. La tension électrique est stabilisée à  $\pm 0.7$  mV ou  $\pm 2$  mV suivant le réglage. [An.Sn.]

**489 – A glass electrode for determining acidity in acetonitrile** (in French). J. Badoz-Lambling, J. Desbarres et J. Tacussel (Laboratoire de chimie analytique, E.P.C.I., 10 rue Vauquelin, Paris, et Sté. Solea, 4 rue Carry, Lyon, France). *Bull. soc. chim. France*, (1962) 53.

Le fonctionnement d'une électrode de verre classique dans un solvant, tel que l'acétonitrile, peut être décrit par la chaîne:

électrode de référence dans l'acétonitrile	solution de pH inconnu dans l'acétonitrile	solution de remplissage dans l'eau	paroi de verre	électrode de référence
				électrode de verre

On constate que dans ce solvant les tensions électriques développées par une telle pile sont peu reproductibles. Pour améliorer leurs résultats, les auteurs proposent de remplir l'électrode par une solution dans l'acétonitrile.

On compare cette électrode à une électrode classique et on constate alors, que dans une solution tampon de pH, la reproductibilité des mesures ( $\pm 10$  mV contre  $\pm 30$  mV) et le temps d'établissement des tensions électriques (5-10 min contre 10-30 min) sont plus favorables dans le cas de l'électrode à remplissage d'acétonitrile. [An.Sn.]

See also abstract no. 466.

### 3. Polarography

**490 – Some electrochemical methods for trace analysis** (in Dutch). J. J. Engelsman (Natuurkundig Laboratorium Philips', Eindhoven, The Netherlands). *Chem. Weekblad*, 58 (1962) 113-115.

In this lecture report, the lower limits of estimation are given for classical polarography (including recently proposed refinements), pulse polarography, voltammetry with rotating mercury coated platinum electrodes, and concentration by deposition on the electrode, followed by anodic stripping. By means of conductometry, it is possible to measure to what extent red phosphorus has been superficially oxidized. In one sample this was found to be 0.1 p.p.m. [H.L.Ki.]

**491 – The theory of oscillographic polarography** (in Russian). L. Ya. Shekun. (University of Kazan, U.S.S.R.). *Zhur. Fiz. Khim.*, 36 (1962) 455–457.

The case where the electric tension changes linearly with time has been considered. An expression is derived for the time derivative of the diffusion current  $di/dt$ . It is shown that the  $di/dt$  curve may be employed for the exact determination of the electric tension peak of the polarograms and for the analysis and estimation of the polarographic reversibility of the electrode reactions. [Ot.So.]

**492 – Theory of alternating current polarography** (in English). H. H. Bauer, W. H. Reinmuth and D. E. Smith (Faculty of Agriculture, University of Sydney, Sydney, Australia, (first author), and Department of Chemistry, Columbia University, N.Y., U.S.A. (co-authors)). *Anal. Chem.*, 33 (1961) 1803–1804.

Some points in the paper by Reinmuth and Smith (*Anal. Chem.*, 33 (1961) 964) concerning the theory of alternating current polarography are questioned by Bauer. Reinmuth and Smith also comment on the points raised by Bauer in his short communication. [Su.Mo.Ce.]

**493 – Anodic stripping polarography using the cathode ray polarograph** (in English). A. P. Mead, A. Parker and E. A. Terry (U.K.A.E.A. Research Group, Chemistry Division, Woolwich Outstation, Great Britain). *Nuclear Sci. Abstract* 16 (1962) 357 *Abstr. No.* 2959.

**494 – Polarographic analysis. Generalities on the method** (in Spanish). V. A. Huertas. *Quim. e ind.*, 7 (1960) 6–11.

A survey of the theoretical basis and literature in the field of polarography, together with a survey of analyses carried out in Spain using this technique. [Ca.Cas.]

**495 – Methods and applications of d.c. polarography** (in German). H. W. Nürnberg and M. von Stackelberg (Max-Planck-Institut für Eisenforschung, Düsseldorf, Deutschland). *J. Electroanal. Chem.*, 2 (1961) 350–387.

Continuing the subject of the review article already published (*J. Electroanal. Chem.*, 2 (1961) 181) the kinetic applications are dealt with in this paper. The subjects considered are: (a), utilization of diffusion controlled limiting currents; (b), kinetic limiting currents with preceding chemical reactions, and with re-production of the depolarizing substance as a result of a subsequent reaction of the depolarization product; (c), utilization of measurements of half-wave electric tensions. The mathematical part is briefly discussed in a short appendix. [Red.]

**496 – The effect of cell resistance on acute polarographic maxima** (in English). I. M. Kolthoff, J. C. Marshall and S. L. Gupta (School of Chemistry, University of Minnesota, Minneapolis, Minn., U.S.A.). *J. Electroanal. Chem.*, 3 (1962) 209–216.

In the absence of external resistance in the circuit, the resistance of a polarographic cell,  $R_{\text{cell}} = R_1 + R_e$ , where  $R_1$  acts as a true internal resistance in the immediate vicinity of the growing mercury drop, and varies with time ( $t$ ) according to the expression  $R_1 = kt^{-1/3}$ . The component  $R_e$  acts as external resistance, is independent of  $t$  and increases with increasing separation between the dropping electrode and the reference electrode. The value of  $k$  is smaller than calculated by Ilkovič and depends on the diameter of the tip of the capillary. With a capillary with an external diameter of the orifice of 0.5 mm the value of  $k$  was in satisfactory agreement with that calculated by Ilkovič. [Authors]

**497 – The so-called tensammetric waves** (in English). A. N. Frumkin and B. B. Damaskin (Institute of Electrochemistry, Academy of Sciences, Moscow, U.S.S.R.). *J. Electroanal. Chem.*, 3 (1962) 36–44.

The term "tensammetry" introduced by Breyer and Hacobian, as well as the mechanism proposed by them to explain the appearance of peaks on the differential capacity-voltage curves in the presence of surface-active substances, has been critically discussed. The value obtained by the method developed by these authors has been shown to be identical to that determined by the comparison method used by Proskurnin and Frumkin. The advantages of the bridge arrangement for the determination of the differential capacity of the electrode have been considered. Curves for the dependence of the differential capacity on the electric tension are given for the case when the desorption process is that of a two dimensional phase transition and for that when, at some electric tensions, a change in the structure of the adsorption layer occurs, unaccompanied by desorption. [Authors]

**498 – A sensitive polarographic technique** (in English). H. B. Mark and C. N. Reilley (Department of Chemistry, University of North Carolina, Chapel Hill, N.C., U.S.A.). *J. Electroanal. Chem.*, 3 (1962) 54–63.

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

**499 – Polarographic reduction of hydrogen on a rhodiated dropping mercury electrode** (in Italian). L. Campanella and E. Scarano (Analytical Chemistry Institute, University of Rome, Italy). *Rass. chim.*, 13 (1961) 13–16.

Rhodium chloride solutions in 0.1 M potassium chloride, after treatment with ion exchange resins, deposit metallic rhodium on the dropping mercury electrode. On this "rhodiated" dropping mercury electrode (RDME) the hydrogen over-tension is greatly decreased; a well developed polarographic wave of hydrogen is obtained at an electric tension of  $-1.35$  V (vs. S.C.E.). The RDME can be very useful in the study of hydrogen reduction, and also as a practical tool for the determination of strong and weak acids. [Su.Mo.Ce.]

**500 – Iodimetric amperometric determination of copper(II)** (in English). D. Singh and V. S. Agarwala (Electrochemical Laboratory, Hindu University, Benares, India). *Current Sci. (India)*, 30 (1961) 12–13.

Iodides and  $Cu^{2+}$  react according to the equation:  $2 Cu^{2+} + 5 I^- = 2 CuI + I_3^-$ , with the precipitation of CuI. The solution can be titrated amperometrically with  $Na_2S_2O_3$  at pH 3.2–5.2, using two polarised electrodes at constant voltage. Ag, Pb,  $Sn^{4+}$ , Bi, Al, Zn and Ni do not interfere. Interference by  $Fe^{3+}$  can be avoided by using alkali pyrophosphate. The error is  $\pm 1.5\%$  and  $Cu^{2+}$  can be determined in amounts up to 6.3 mg. [Gio.Ser.]

**501 – Micromethod for separation and determination of calcium, strontium and barium** (in German). A. Tockstein and V. Novák (Technische Hochschule für Chemie, Pardubice, Tschechoslovakei). *Mikrochim. Acta*, (1962) 142–154.

Addition of Co(II) to a strongly ammoniacal solution, containing  $SO_4^{2-}$ , ethylene diaminetetraacetate (EDTA),  $Ba^{2+}$ ,  $Sr^{2+}$  and  $Ca^{2+}$  brings about precipitation of  $BaSO_4$ . In the presence of ethanol  $SrSO_4$  is also precipitated. After separation of the different sulphates by centrifuging, Ca, Sr and Ba are determined by observation of the heights of the two polarographic waves which arise after introduction of the alkaline earth sulphate into a solution of the silver EDTA complex. The relative error amounts to 3%. The method seems to be rather laborious. [H.L.Ki.]

**502 – Determination of cadmium and nickel in the active mass of alkaline accumulators by amperometric titration** (in Russian). E. G. Novakovskaya (State Research Institute of the Accumulator Industry, U.S.S.R.). *Zavodskaya Lab.*, 28 (1962) 28–29.

The determination of nickel in the presence of large amounts of cadmium is based on precipitation of nickel by dimethylglyoxime, and titration of cadmium by EDTA in the presence of the nickel precipitate. Nickel is determined by reverse titration of excess dimethylglyoxime by a standard nickel solution. The supporting electrolyte is ammonia–ammonium chloride. Cd is determined with a relative error of 0.3%, Ni with an error of 3%. [Ot.So.]

**503 – Use of amino compounds in the polarography of inorganic substances. XII. Determination of Cd, Pb and Tl in indium** (in German). J. Doležal, V. Petrus and J. Zýka (Institut für analytische Chemie, Karlsuniversität, Prag, Tschechoslovakei). *J. Electroanal. Chem.*, 3 (1962) 274–277.

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-hydroxyäthylamin mit 0.1 M NaOH als Elektrolyt ist beschrieben. [Authors]

**504 – Determination of aluminium in thorium compounds by linear sweep oscillographic polarography** (in English). T. M. Florence (Australian Atomic Energy Commission Research Establishment, Lucas Heights, N.S.W., Australia). *Anal. Chem.*, 34 (1962) 496.

The polarographic reduction of the complex of aluminium with 5-sulpho-2',4',2-trihydroxyazobenzene (Superchrome Garnet Y) is used for the determination of Al in thorium compounds. Of 35 ions investigated only Fe, Ni, Pb, and V interfere.  $1 \mu g$  of Al can be detected in 1 g Th with an accuracy of 3–7%. Th is masked by acetate. The recommended procedure is described in detail.

The measurements are made with a Southern Instruments Cathode Ray Polarograph, Model K 1000. The optimum pH is 5.75, and must be carefully controlled. Some polarograms of the complex are shown. [Kl.Gr.]

**505 – Polarographic determination of thallium in an atmospheric sample** (in English). A. S. Landry (International Cooperation Administration, Lima, Peru, South America). *Am. Ind. Hyg. Assoc. J.*, 21 (1960) 407–413.

A method is described in which thallium can be determined polarographically in the presence of Pb. The method is based on the use of 2.7 M CaCl<sub>2</sub> as supporting electrolyte and of EDTA as chelating agent. Tl can be determined in concentrations ranging from 10–50 µg per ml in the presence of more than 20 µg per ml of Pb. If Fe is present, Tl must be extracted with ethyl ether from a solution which has been made 1 M in HBr. Pb and Tl can be determined together. [Gio.Ser.]

**506 – Polarographic investigation of complexes participating in the electrode reaction in the system Ti(IV)–Ti(III) in hydrochloric acid media** (in Russian). A. G. Stromberg and A. I. Kartushinskaya (Polytechnic Institute, Tomsk, U.S.S.R.). *Izvest. Sibir. Otdel. Akad. Nauk S.S.S.R.*, [11] (1961) 88–97.

Experiments were carried out in solutions of the system Ti(IV)–Ti(III) in hydrochloric acid, varying in the hydrogen and chlorine ion concentrations. The following complexes were found to be present in the solution: Ti(OH)<sub>2</sub>Cl<sub>2</sub>, Ti(OH)Cl<sub>2</sub><sup>+</sup> and Ti<sup>3+</sup>. The following take part in the electrode reaction: Ti(OH)Cl<sub>2</sub><sup>+</sup> and Ti(OH)Cl<sup>+</sup>. Expressions were derived for the standard electric tension of the electrode reaction. [Ot.So.]

**507 – Polarographic determination of Pb<sup>2+</sup> and Sn<sup>2+</sup> ions present together in solution** (in French). J. Cantacuzene and R. Zermizoglou (Laboratoire de chimie, Ecole Normale Supérieure, 24 rue Lhomond, Paris, France). *Bull. soc. chim. France*, (1962) 283–284.

Les tensions électriques de demi-vague des ions Pb<sup>2+</sup> et Sn<sup>2+</sup> ne sont pas suffisamment séparées pour qu'on puisse les doser conjointement par polarographie. En milieu acide citrique 1 M, malgré une différence de 0.26 V entre les tensions électriques de demi-vague (pris séparément), les auteurs observent encore une interférence des deux vagues. Par contre, en ce milieu, l'étain(II) s'oxyde facilement par l'air en étain(IV). Celui-ci ne se réduit plus à la même tension électrique que le plomb(II). Deux polarogrammes, l'un avant, l'autre après barbotage d'air, permettent donc de déterminer successivement la somme des courants de diffusion, puis le courant de diffusion dû au plomb. Le dosage est rapide et il permet de doser des solutions contenant jusqu'à 100 fois plus de Sn<sup>2+</sup> que de Pb<sup>2+</sup>. [An.Sn.]

**508 – Amperometric titration of small amounts of thorium with EDTA** (in Russian). P. N. Palei and N. I. Udal'tsova. *Trudy Komissii Anal. Khim., Akad. Nauk S.S.S.R.*, 11 (1960) 299–305.

The solution containing Th (0.3–15.0 mg) is neutralised to pH 2.0–3.5 with aqueous NH<sub>3</sub>, and titrated with 0.1, 0.05 or 0.005 M EDTA. Two polarisable Pt electrodes are used, and the oxidation current of EDTA at 0.4–0.5 V is measured after 3–5 min, stirring after each addition. The current is measured during stirring. Al, UO<sub>2</sub><sup>2+</sup> and rare elements do not interfere. Monazite sand can be analysed after separation of rare earth elements with oxalic acid. [Gio.Ser.]

**509 – Polarographic microdetermination of arsenic made insoluble by treatment with Cl<sub>2</sub> and SO<sub>2</sub>** (in French). L. Vignoli, B. Cristau et F. Gouezo (Laboratoire de pharmacie chimique et de toxicologie, Faculté mixte de Médecine et de Pharmacie de Marseille, France). *Chim. anal.*, 44 (1962) 3–6.

Les auteurs décrivent un mode opératoire permettant de doser par polarographie l'arsenic, isolé à l'état de métalloïde. L'arsenic est oxydé par le chlore en As(V) puis réduit par SO<sub>2</sub> en As(III). Après une élimination minutieuse du SO<sub>2</sub> dont la vague polarographique interfère avec la première vague de l'arsenic ( $E_{1/2} = -0.43$  V), il est possible de doser jusqu'à 20–25 µg d'arsenic par le tracé d'un polarogramme en milieu tartrique. [Bad.Lam.]

**510 – Cyclic voltammetry of aqueous solutions of chromium compounds on the stationary hanging mercury drop electrode. Chloride complexes of Cr(III)** (in Polish). W. Kemula and E. Rakowska (Department of Inorganic Chemistry, The University, Warsaw, Poland). *Roczniki Chem.*, 36 (1962) 203–213.

The behaviour of Cr(III) and Cr(II) complexes in different electrolytes, KCl, CaCl<sub>2</sub>, HCl, KBr, K<sub>2</sub>SO<sub>4</sub> and HClO<sub>4</sub> was investigated by means of cyclic voltammetry on the stationary hanging mercury drop electrode with polarographic and oscillographic recording. The influence of pH, gelatin,

temperature and frequency variations of the applied voltage were studied. It was observed that reduction of  $(\text{Cr}(\text{H}_2\text{O})_4)^{3+}$  in solutions containing  $\text{Cl}^-$  and  $\text{Br}^-$  ions results in formation of different kinds of complexes, in which one or two  $\text{H}_2\text{O}$  molecules are replaced by halogen ions. The products formed are present in the vicinity of the electrode surface. The reduction of the secondarily formed complexes,  $(\text{Cr}(\text{H}_2\text{O})_5\text{Cl})^{2+}$  or  $(\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2)^+$ , takes place at more positive electric tensions than reduction of the initial compound, and therefore a new maximum appears in the second cycle. The system  $\text{Cr}(\text{III})(\text{H}_2\text{O})_n\text{X}_m/\text{Cr}(\text{II})$  was found to be reversible in 0.1 N KBr, almost reversible in 10 N  $\text{CaCl}_2$ , and more or less irreversible in other electrolytes studied. [Ad.Hu.]

**511 – Polarographic behaviour of chromate ion. I. Reaction mechanism and influence of the supporting electrolyte** (in French). J. J. Tondeur, A. Dombret and L. Gierst (Faculté des Sciences, Université Libre de Bruxelles, Belgique). *J. Electroanal. Chem.*, 3 (1962) 225–262.

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. [Authors]

**512 – Polarographic determination of selenium in urine** (in English). A. G. Faulkner, E. C. Knobloch and W. C. Purdy (Division of Nuclear Medicine and Chemistry, Walter Reed Army Institute of Research, Washington D.C., U.S.A.). *Clin. Chem.*, 7 (1961) 22–29.

The urine sample is evaporated to dryness, and heated with  $\text{HNO}_3$  and  $\text{H}_2\text{SO}_4$  until fuming.  $\text{H}_2\text{O}_2$  is added, and heating is continued to destroy the excess of  $\text{H}_2\text{O}_2$ . The solution is diluted with  $\text{H}_2\text{SO}_4$  to a final concentration of 3 M  $\text{H}_2\text{SO}_4$ . After deaeration with nitrogen, the polarogram is recorded. The first wave is due to Se and the diffusion current is proportional to the concentration. Standard solutions are prepared by treating pure Se in the same way as the urine sample. The Se content of urine can be kept constant for four days if the sample is acidified to 1 M  $\text{HNO}_3$ . [Gio.Ser.]

**513 – A polarographic study of some complexes of molybdenum** (in English). E. W. Zahnow and R. J. Robinson (Department of Chemistry, University of Washington, Seattle, Wash., U.S.A.). *J. Electroanal. Chem.*, 3 (1962) 263–273.

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. [Authors]

**514 – Application of polarography to organic chemistry** (in English). P. Zuman (Polarographic Institute, Czechoslovak Academy of Science, Prague, Czechoslovakia). *J. Electroanal. Chem.*, 3 (1962) 157–168.

A review concerning various applications of polarography in the field of organic chemistry: analysis, homogenous reactions, organic electrode processes, reactivity and structure, and synthesis are considered. [Red.]

**515 – A new polarographic method for the microdetermination of chloropicrin in air** (in English). B. Berck and J. Solomon (Canadian Department of Agriculture Research Station, Winnipeg, Manitoba, Canada). *Anal. Chem.*, 34 (1962) 514.

A rapid polarographic method for the direct determination of chloropicrin in air is described. The polluted air is drawn through a trap with a mixture of 940 ml 85% methanol, 50 ml 1% gelatin maximum suppressor solution and 10 ml 8 N nitric acid. The solution is then polarographed. A special silver–silver chloride comparison electrode is used. The details of construction for this electrode are given. The overall precision of the method is 1.1–5% in the concentration range  $4.27 \cdot 10^{-3}$ – $1.22 \cdot 10^{-5}$  M. [Kl.Gr.]

**516 – Use of amino compounds in the polarography of inorganic compounds. X. Polarographic behaviour of some ions in 1-amino-3-propanol, bis-(2-hydroxypropyl)-2-hydroxyethylamine and bis-(2-hydroxybutyl)-2-hydroxyethylamine** (in German). J. Doležal, V. Petrus and J. Zýka (Lehrstuhl für analytische Chemie der Karlsuniversität, Prag, Tschechoslowakei). *J. Electroanal. Chem.*, 3 (1962) 91–97.

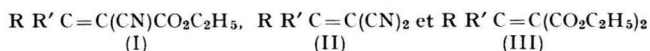
The dissociation constants of 1-amino-3-propanol, bis-(2-hydroxypropyl)-2-hydroxyethylamine and bis(2-hydroxybutyl)-2-hydroxyethylamine have been measured and calculated. The behaviour of a large number of elements has been investigated in media containing these amino-alcohols. [Authors]

**517 – Use of amino compounds in the polarography of inorganic compounds XI. Polarographic behaviour of Mn and Fe in media of bis-(2-hydroxypropyl)-2-hydroxyethylamine, bis-(2-hydroxybutyl)-2-hydroxyethylamine and alkali hydroxide** (in German). J. Doležal, V. Petrus and J. Zýka (Lehrstuhl für analytische Chemie der Karlsuniversität, Prag, Tschechoslowakei). *J. Electroanal. Chem.*, 3 (1962) 169–181.

The polarographic behaviour of manganese, iron and several other ions was investigated in a medium consisting of bis-(2-hydroxypropyl)-2-hydroxyethylamine, bis-(2-hydroxybutyl)-2-hydroxyethylamine and alkaline hydroxide. It was found that complexes of bi- and trivalent manganese and iron behave, under certain conditions at the dropping mercury electrode, as reversible redox systems. The complex-forming electrolyte mentioned can be used for the polarographic estimation of manganese and iron, in addition to a whole series of other ions. The method was tested by the analysis of manganese ore and siderite. (See abstract no.516.) [Authors]

**518 – Sur la réduction polarographique de quelques cyano-2 propène-2-oates d'éthyle substitués en 3 et des dinitriles et diesters correspondants** (en français). M. Bargain (Groupe de Recherches de Physicochimie structurale, Faculté des Sciences, Rennes, France). *Compt. rend.*, 254 (1962) 130–132.

L'auteur étudie la réduction polarographique en milieu hydroalcoolique de la liaison éthylénique des dérivés suivants:



où R = C<sub>6</sub>H<sub>5</sub> et R' = H, C<sub>6</sub>H<sub>5</sub> pour I, II et III, et R' = CH<sub>3</sub>, C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub> pour I et II. On observe en milieu acide (pH < 6) une vague à deux électrons dont le E<sub>1/2</sub> varie de 0.05 V par unité de pH. En milieu alcalin le dédoublement en deux vagues à un électron est net pour certains composés. Un tableau indique les valeurs des tensions électriques de demi vague à pH 8.9. Une étude spectrophotométrique dans l'ultraviolet permet de confirmer que le dédoublement de la vague à deux électrons est lié à la stabilité du radical formé durant la première étape de réduction. Les effets polaires des substituants R et R' peuvent dans certains cas être déduits des valeurs de la tension électrique de demi vague. [An.Sn.]

**519 – Polarographic behaviour of thiocholine, acetylthiocholine and cholinedisulphide** (in German). V. Fišerová-Bergerová (Institute for the Hygiene of Work and Professional Diseases, Prague, Czechoslovakia). *Collection Czechoslov. Chem. Commun.*, 27 (1962) 693–700. Thiocholine forms an anodic polarographic wave, corresponding to formation of the mercury salt. In the oxidised form the disulphide bond is reduced. Glutathione may be employed as a model substance for the determination of thiocholine. [Ot.So.]

**520 – Polarography of diethyldithiocarbamate used as titrant with a rotating dropping mercury indicator electrode** (in English). W. Stricks and S. K. Chakravarti (Department of Chemistry, Marquette University, Milwaukee, Wisc., U.S.A.). *Anal. Chem.*, 34 (1962) 508. The rotating dropping mercury cathode can be used as an indicator electrode for complexometric titration with diethyldithiocarbamate (RSH). Two methods are described. The first uses the decrease in current caused by reduction of the uncombined metal ion during the titration. The second is based on the anodic diffusion current caused by excess RSH after reaching the end-point of the titration. Polarograms of the RSH oxidation are given and the polarographic behaviour of the dye is investigated. This method of indication can be used for the determination of Hg(II), Tl(I), Cu(II), Zn, Sn(II), Pb, Ni(II), Fe(III) and Cd. The compositions of the supporting electrolyte for the various ions to be determined are given. The average error in the titration of Hg, Pb, Cu, and Zn is below 1%. [Kl.Gr.]

**521 – Polarographic studies on the reduction and stability of ω-nitrostyrene.** L. Holleck and D. Jannakoudakis (Institut für physikalische Chemie, Universität Hamburg, Deutschland). *Z. Naturforsch.*, 16B (1961) 396–398.

ω-Nitrostyrol nimmt mit seinem komplizierten Stufenbild eine Mittelstellung zwischen aromatischen und aliphatischen Nitroverbindungen ein. pH < 3 werden (4 + 2) Elektronen, pH > 3 nur 4 Elektronen aufgenommen, wobei der Austausch des 1. Elektrons reversibel erfolgt (Campherzusatz). In alkalischem Medium erfolgt Bildung der Acinitroform, Polymerisation und Hydrolyse, wobei Benzaldehyd entsteht und einige neue Stufen hinzukommen. Auch u.v. Strahlung bewirkt Polymerisation. [He.Be.]

**522 – Polarographic properties of some organic compounds of phosphorus** (in Russian). L. M. Shapiro. *Doklady Akad. Nauk Belorus. S.S.S.R.*, [4] 3 (1959) 146–149.

Polarography was carried out in aqueous acetone, buffered at various pH values between 3-11; the addition compound of diethylphosphorous acid with *m*-nitrobenzalanine (a) with *p*-nitrobenzalanine (b) and with thiphos (c) showed sharp waves whose heights are proportional to concentration and pH independent. The values of the half-wave electric tension increase in going from acid to neutral solution, but remain constant in alkali solution. Other waves appear at pH 1.8 and pH 3. The solution of (b) is light sensitive; the half-wave electric tension of (c) depends upon concentration. [Red.]

**523 - Kinetics of the reduction, polarography and infra-red spectra of substituted nitrodiphenyl sulphides and sulphones** (in German). R. Zahradník (Institute for the Hygiene of Work and Professional Diseases, Prague, Czechoslovakia). *Collection Czechoslov. Chem. Commun.*, 27 (1962) 525-532.

The kinetics of reduction with Ti(III) chloride, the polarographic half-wave electric tensions and i.r. frequencies of nitrodiphenyl sulphides were investigated. The results obtained show that the -S or -SO<sub>4</sub> groups transmit no, or only slight, resonance interaction between the two benzene rings. Half-wave electric tensions of 22 compounds of this class, obtained in solutions containing 1.00 ml of a  $1 \cdot 10^{-3}$  M ethanolic stock solution and 9.00 ml buffer in 50% ethyl alcohol, are tabulated. [Ot.So.]

**524 - Polarography of heterocyclic aromatic compounds. XIII. Polarographic fission of carbon-halogen bonds in monohalogenopyridines** (in English). J. Holubek and J. Volke (Research Institute of Natural Drugs, Prague, and Polarographic Institute, Czechoslovak Academy of Sciences, Prague, Czechoslovakia). *Collection Czechoslov. Chem. Commun.*, 27 (1962) 680-692.

Isomeric halogenopyridines are reduced irreversibly at the dropping mercury electrode, two electrons being accepted. The reaction products are a halogen ion and a pyridine molecule. With the exception of iodopyridines, only the cations are affected by this reaction, up to -1.8 V. The pH-dependence of the half-wave electric tensions has the shape of a sigmoid. The course of reduction of the iodopyridine free base is different. Substitution of chloride by bromide, and further by iodide, facilitates reduction, as well as the transition from the free base to the cation and the quaternary derivative. [Ot.So.]

**525 - Polarographic investigation of N-oxy-N-methylpiperidine. Kinetic waves of N-oxides** (in Russian). S. G. Mairanovskii, N. Y. Barashkova and F. D. Alashev (Institute of Organic Chemistry, Academy of Sciences, U.S.S.R.). *Zhur. Fiz. Khim.*, 36 (1962) 562-566.

It was shown that in an alkaline medium the N-oxy-N-methylpiperidine wave is limited by the rate of transition of the electrochemically inactive basic form to the protonized acid form. The kinetic wave of this compound is the result of the preceding chemical reaction occurring in the bulk of the solution ("space-wave"). The rate constants of the protonization of N-oxy-N-methylpiperidine on reaction with boric acid ( $k_B = 1.6 \cdot 10^3$  l mole<sup>-1</sup> sec<sup>-1</sup>) and with the hydrogen ion ( $k_H^+ = 7 \cdot 10^9$  l mole<sup>-1</sup> sec<sup>-1</sup>) at  $t = 25^\circ$  were calculated from experimental data. The kinetic wave of N-oxy-pyridine is limited by the reaction taking place with the adsorbed N-oxide participating, i.e. to a partially "surface" kinetic wave. [Ot.So.]

**526 - Use of organic reagents in amperometric titration of some rare elements** (in Czech). F. Vydra. *Chem. listy*, 56 (1962) 372-374.

A brief review, based on 28 literature references. The use of 8-oxyquinoline, *m*-nitrophenylarsinic acid, cupferron and EDTA is reviewed. The elements determined, and in some cases conditions of the titration, are dealt with. [Ot.So.]

**527 - Polarographic study of N-oxides** (in German). G. Horn (Institut für Mikrobiologie und experimentelle Therapie, Jena, Deutschland). *Monatsber. Deut. Akad. Wiss.*, 3 (1961) 386-394.

Ausgehend von bekannten N-Oxyden des Chinolins, Chinaldins, Picolins u.a. wurden insbesondere cytotatisch wirksame Derivate polarographiert. Abgesehen von katalytischen Wasserstoffwellen, bestehen die Polarogramme aus mehreren, zumeist einelektronigen Teilstufen der protonisierten Depolarisatoren. Der normale Grenzstromverlauf wird häufig durch Maxima und Adsorptionseffekte gestört. [He.Be.]

**528 - Polarographic behaviour of actinomycins** (in Slovakian). M. Fedorenko and H. Berg (Chemical Institute, Slovakian Academy of Sciences, Bratislava, Czechoslovakia). *Chem. zvesti*, 16 (1962) 28-43.

The polarographic behaviour of phenoxazone, actinomycin chloride and chloractinomycin chloride



is described. Phenoxazone exhibits reversible reduction under all conditions; the other two substances exhibit reversibility only in the protonised form. At concentrations over  $5 \cdot 10^{-5} M$  the cathodic wave splits into two, as a result of adsorption of the actinomycins on the surface of the drop electrode, by their peptide ends, in the vicinity of electrocapillary zero. [Ot.So.]

**529 – The polarographic determination of dyes used for the colouration of food** (in Italian). E. Cerma. *Rass. chim. per chim. e ind.*, 12 (1960) 13–60.

The possibility of quantitative polarographic determination of 13 dyes, authorized by Italian legislation, for colouring food was investigated, with special reference to "Tramonto" yellow, solid red E, azorubine, amaranth, flame-colour 4 R and 6 R, scarlet GN, tartrazine, bright black RN, erythrosin, quinoline yellow, indigotin and patent white V. The apparatus is described (AME polarographic apparatus with photographic recorder) and the best conditions for qualitative and quantitative analysis are given for each dye studied in this paper. [Fr.Cla.]

See also abstracts nos. 458, 465, 478, 479, 480, 486.

#### 4. Potentiometry

**530 – Experimental evaluation of liquid-junction electric tension** (in English). I. V. Nelson and R. T. Iwamoto (Department of Chemistry, University of Kansas, Lawrence, Kan., U.S.A.). *Anal. Chem.*, 33 (1961) 1795–1796.

The 4,7-dimethyl-1,10-phenanthroline ferric-4,7-dimethyl-1,10-phenanthroline ferrous couple is better than the rubidium couple for the experimental evaluation of liquid-junction electric tensions. Half-wave electric tension values observed for the oxidation of ferrous 4,7-dimethyl-1,10-phenanthroline at a rotating platinum electrode in 13 different solvents are reported. Differences in the observed values for the different solvents are ascribed to differences in liquid-junction electric tensions. [Su.Mo.Ce.]

**531 – The formation of membrane potentials with the help of difficultly soluble salts** (in German). L. Grahm und C. H. Hertz (Physikalisches Institut der Universität Lund, Schweden). *Z. Elektrochem.*, 65 (1961) 185–192.

Wenn die Oberseite einer waagrecht zwischen zwei, mit der gleichen Elektrolytlösung gefüllten Zellen liegenden Ionenaustauschermembran mit einem schwerlöslichen Salz bedeckt wird, entsteht eine elektrische Spannung. Diese kann Werte bis zu 40 mV annehmen, wenn die Konzentration der Elektrolytlösung beiderseits der Membran etwa  $10^{-3} N$  beträgt. Es wird bewiesen, dass ein vorwiegend nach filmkinetischen Gesetzen ablaufender Austauschprozess stattfindet. Das schwerlösliche Salz wird aufgelöst und reagiert unter der Wirkung der Austauschermembran mit der in diese eingedrungene Elektrolytlösung. Das entstandene Membranpotential beruht auf einer Änderung des Donnanpotentials infolge des Ionenaustritts aus der Membran. Die Autoren führten Messungen der elektrischen Spannungen in Abhängigkeit von der Zeit mit Hilfe von Kalomel-Elektroden durch und verfolgten die Änderungen der Ionenkonzentration flammenphotometrisch und durch Leitfähigkeitsmessungen. Die Bildung hydrolysierender Substanzen, wie z.B.  $K_2CO_3$  wurde auch durch pH-Indikatoren nachgewiesen. Der Effekt wird qualitativ erklärt und auch quantitativ behandelt, die theoretisch berechneten Membranpotential-Zeit-Kurven werden mit den experimentellen verglichen. Das beobachtete Membranpotential kann zur Erklärung des geoelektrischen Effektes bei Pflanzen dienen, wenn man annimmt, dass schwerlösliche Zellbestandteile sedimentieren und die darunter liegende Zellwand (Membran) bedecken. [He.We.]

**532 – Studies of the copper(II)-alanine and phenylalanine systems in aqueous solution. Dissociation and formation constants as a function of temperature** (in English). R. M. Izatt, J. W. Wrathall and K. P. Anderson (Department of Chemistry, Brigham Young University, Provo, Utah, U.S.A.). *J. Phys. Chem.*, 65 (1961) 1914–1915.

The systems were studied by pH titration using a pH meter. The dissociation constants and the formation constants are given at temperatures from 0–40°, and  $\Delta S^\circ$  and  $\Delta H^\circ$  were calculated. [D.S.Ru.]

**533 – Standard electrode tensions of alkaline earth metals in methanol** (in Polish). B. Jakuszcwski and S. Taniewska-Osińska (Department of Physical Chemistry, The University, Łódź, Poland). *Roczniki Chem.*, 36 (1962) 329–334.

The standard electric tensions of cells containing the electrodes in aqueous and methanolic solutions of the three metals have been determined. The cells were of the following type: Pb,  $\text{PbCO}_3$ ,  $\text{MeCO}_3$  ( $\text{MeX}_2$ ),  $\text{Hg}_2\text{X}_2$ , Hg in solution, where X represents Cl or Br. Using the known values of the standard free energy of formation of substances taking part in electrode reactions, the standard electric tensions in water and methanol were calculated. Their values are as follows: for water solutions- $E^\circ_{\text{Ca/Ca}^{2+}} = -2.868 \text{ V}$ ,  $E^\circ_{\text{Sr/Sr}^{2+}} = -2.886 \text{ V}$  and  $E^\circ_{\text{Ba/Ba}^{2+}} = -2.912 \text{ V}$ ; for methanol solutions,  $E^\circ_{\text{Ca/Ca}^{2+}} = -2.929 \text{ V}$ ,  $E^\circ_{\text{Sr/Sr}^{2+}} = -2.938 \text{ V}$  and  $E^\circ_{\text{Ba/Ba}^{2+}} = -2.943 \text{ V}$ . [Ad.Hu.]

**534 – Foreign cation effects on measured stability constants** (in English). J. F. Tate and M. M. Jones (Department of Chemistry, Vanderbilt University, Nashville, Tenn., U.S.A.). *J. Phys. Chem.*, 65 (1961) 1661–1662.

The stability of a  $\text{CdNO}_3^+$  complex was determined in the presence of Sr, Ca, Na, Nd, Al, La and Li nitrates. The stability constant was found to vary 7 fold (1.063–0.142) from Sr to Li, indicating that it was very dependent on the specific nitrate present. [D.S.Ru.]

**535 – Electrometric titration of choline phosphoric acid. Influence of the  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$  and  $\text{Zn}^{2+}$  ions** (in French). J. Attias (Laboratoire de chimie biologique, Faculté des Sciences, Montpellier, Herault, France). *Compt. rend.*, 254 (1962) 946–948.

Un titrage potentiométrique à l'électrode de verre d'une solution d'acide cholinephosphorique,  $^+\text{N}(\text{CH}_3)_3\text{—CH}_2\text{—O—PO}_3\text{H}_2$ , (symbolisé par le sigle PC) permet à l'auteur de déterminer les constantes de dissociation de cet acide,  $\text{p}K'_1 = 1.47$  et  $\text{p}K'_2 = 5.84$ . La présence d'ions  $\text{Mg}^{2+}$  et  $\text{Ca}^{2+}$ , et dans une moindre mesure d'ions  $\text{Na}^+$ , fait apparaître une diminution du pH de demi-neutralisation de la deuxième acidité. La variation de ce pH de demi-neutralisation en fonction de la concentration du cation  $M^{2+}$  permet d'admettre que l'acide cholinephosphorique forme avec les ions  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$  et  $\text{Zn}^{2+}$  des complexes du type,  $\text{PCM} \rightleftharpoons \text{PC}^{2-} + M^{2+}$ . [Bad.Lam.]

**536 – Potentiometric determination of stability constants of  $\text{VO}^{2+}$ –ascorbic acid complexes** (in Polish). A. Sobkowska and J. Minczewski (Department of Analytical Chemistry, Institute of Nuclear Research, Warsaw, Poland). *Roczniki Chem.*, 36 (1962) 17–26.

The consecutive stability constants of  $\text{VO}^{2+}$  complexes with ascorbic acid were determined using a previously described method (*Roczniki Chem.*, 35 (1961) 47). The measurements of electric tensions in a cell system with two glass electrodes were performed for the ionic strength  $\mu = 1.0$ , maintained by addition of  $\text{NaClO}_4$ . In the presence of ascorbic acid, hydrolysis occurs at a pH higher than 3.85, and all measurements were performed in the range below this value. For mononuclear complexes the following stability constants were evaluated:  $\text{p}\beta_1 = 1.50 \cdot 10^2$ ;  $\text{p}\beta_2 = 4.5 \cdot 10^2$ ;  $\text{p}\beta_3 = 2.5 \cdot 10^4$ . These values are lower than corresponding values for the uranyl ion. This can be attributed to a higher positive charge on the uranyl ion. [Ad.Hu.]

**537 – Potentiometric study of the oxidation of trivalent molybdenum by lead tetraacetate** (in English). A. Berka, J. Doležal, I. Nemeč and J. Zýka (Department of Analytical Chemistry, Charles University, Prague, Czechoslovakia). *J. Electroanal. Chem.*, 3 (1962) 278–282.

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  $5\text{--}7 \text{ N}$  HCl solutions Mo(III) is quantitatively oxidised to Mo(VI), and in  $8\text{--}10 \text{ N}$  HCl solutions to Mo(V). [Authors]

**538 – Spectrophotometric and potentiometric determination of uranium as the chelate of 8-hydroxyquinoline in a mixed solvent. Fresenius systematic analysis of the cations and use of 8-hydroxyquinoline.** A. R. M. Al-Salihi. *Dissertation Abstr.*, 21 (1961) 2091–2092.

Derivatives of 8-hydroxyquinoline with Al,  $\text{Fe}^{3+}$ , Bi,  $\text{UO}_2^{2+}$  and Ti were prepared, and the solubilities in acetone, ethanol, and their mixtures with water were studied at  $26^\circ\text{--}27^\circ$ . Uranium can be determined by spectrophotometry at  $460 \text{ m}\mu$  in acetone–water solution. The Al complex can be titrated potentiometrically in ethanol–water with HCl, with an error of 2.75%. The uranyl complex can be titrated satisfactorily in acetone–water with NaOH with an error of 0.5%. The preparation of the U complex from ores, containing small amounts of U, is discussed. The complexes of the cations that can be precipitated from acetic acid–ammonium acetate buffers, and their determination, have been studied. Silver, Hg<sup>+</sup> and  $\text{Pb}^{2+}$  can be identified by the effect of u.v. light on their chlorides, but the complexes with 8-hydroxyquinoline can also be used. Spot tests are described for  $\text{Cd}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Al}^{3+}$ . [Gio.Ser.]

**539 – Potentiometric determination of bromide and thiocyanate in one operation with silver nitrate and the silver electrode** (in German). M. Scheibitz (Agfa Aktien Gesellschaft, Wolfen, Deutschland). *Z. wiss. Phot.*, 54 (1960) 46–51.

The separation of bromide and  $\text{SCN}^-$ , which is impossible by potentiometric titration with  $\text{AgNO}_3$  in aqueous solution, can be effected by adding gelatin (0.05–0.5%) to the solution. Two breaks appear in the titration curve when the concentration of  $\text{Br}^-$  is  $\geq$  the concentration of  $\text{SCN}^-$ . The theoretical reasons for this are discussed.  $\text{Cl}^-$  can also be determined in gelatin solution, provided that correction is made for the  $\text{Cl}^-$  content of gelatin. Applications in the analysis of photographic developers are shown. [Gio.Ser.]

**540 – Acetic anhydride as a non-aqueous ionising solvent. III. Potentiometric titration and estimation of the ionic product of acetic acid-free acetic anhydride from potential measurements** (in German). G. Jander and H. Surawski (Anorganisch-Chemisches Institut der Technischen Universität, Berlin, Deutschland). *Z. Elektrochem.*, 65 (1961) 527–530.

Die in einer vorangegangenen Arbeit konduktometrisch und präparativ verfolgten neutralisationsanalogen Reaktionen in reinstem Essigsäureanhydrid wurden jetzt auch potentiometrisch untersucht. Hierzu wurde eine „gebremste“ Goldelektrode mit praktisch veränderter Diffusion als Vergleichselektrode, eine gewöhnliche Goldelektrode als Indikatorelektrode verwendet und damit die Berührung der Lösungen mit einem wässrigen Vergleichssystem wie etwa der Kalomelektrode vermieden. Die gebremste Goldelektrode spricht auf Acetationen konzentrationsrichtig an. Die potentiometrischen Titrationskurven entsprechen ihrem Typ nach analogen Neutralisationskurven wässriger Lösungen; so ist z. B. die potentiometrische Titrationskurve von Kaliumacetat mit Acetyl bromid in Essigsäureanhydrid derjenigen einer mittelstarken Base mit einer schwachen Säure in Wasser analog. Auf Grund von Spannungsmessungsreihen zwischen reinstem Essigsäureanhydrid und dem basenanalogen Kaliumacetat in verschiedenen Konzentrationen wurde das Ionenprodukt dieses Lösungsmittels mit Hilfe der Nernst'schen Gleichung nach Einsetzen der „wahren“ Acetationenaktivität

$$a_{\text{Ac}^-} = c_{\text{Ac}^-} \alpha f$$

abgeschätzt auf den Wert  $P = 3 \cdot 10^{-15}$  bei  $20^\circ$ .

[He.We.]

**541 – Application of constant current potentiometry to non-aqueous titration of organic bases** (in English). G. R. Svoboda (Chemistry Department, University of Wisconsin, Madison, Wis., U.S.A.). *Anal. Chem.*, 33 (1961) 1638–1640.

The method of constant current non-aqueous potentiometric titration of organic acids (I. Shain and G. R. Svoboda, *Anal. Chem.*, 31 (1959) 1857) can be extended to the non-aqueous titration of organic amines. Peak-shaped titration curves (electric tension vs. titrant volume) allow the determination of the end-point with a precision and accuracy which are comparable to, or better than, those reported for any zero current potentiometric or indicator titrations of bases in non-aqueous solvent. The technique can be adapted to automatic titration. Perchloric acid in *m*-cresol is used as a titrant solution for the determination of a series of amines, using *m*-cresol and acetonitrile (1:1) as solvent. [Su.Mo.Ce.]

**542 – Investigation of the influence of phenyl substituents in the benzene ring. II. Phenyl derivatives of aniline** (in Polish). W. Polaczkowa, N. Porowska and B. Dybowska (Department of Organic Chemistry, Politechnika, Warsaw, Poland). *Roczniki Chem.*, 36 (1962) 41–50.

The dissociation constants of some phenyl derivatives of aniline in 75% aqueous ethanol at  $22^\circ$  have been determined. The following  $\text{p}K'$  values were obtained: *p*-phenylaniline, 4.37; 3,5-diphenylaniline, 4.34; and 3,4,5-triphenylaniline, 4.29. For comparison, the  $\text{p}K'$  values for the following amines were determined: aniline, 4.64; *m*-toluidine, 4.81; *p*-toluidine, 5.19; 3,5-dimethylaniline, 4.97; 3,4,5-trimethylaniline, 5.45; and 3,5-dimethyl-4-ethylaniline, 5.38. The value of  $\rho = +3$  was calculated for these conditions. In addition, the u.v. spectra of all compounds were recorded. From these data it was concluded that the substituents in positions 3, 4 and 5 show a lack of additivity for the plot of  $\log(K/K_0)$  vs.  $\sigma$ . The basicity is lowered due to simultaneous inductive and resonance effects of the phenyl groups. These groups in the 3,4 and 5 positions show only a small inductive effect. [Ad.Hu.]

**543 – Reductometric determination of hydroxytriphenylmethane dyes with vanadium sulphate** (in Slovakian). M. Matrka and Z. Sagner (Research Institute of Organic Syntheses, Pardubice-Rybitví, Czechoslovakia). *Chem průmysl*, 11 (1961) 135.

The method has been applied to the determination of aurine, eriochrome azuro (C.I. Mordant Blue I), chrome blue R (C. I. Mordant Blue 42) chromoxane brown 5 R (C. I. Mordant Brown 26), and naftochrome azurine B (C. I. Mordant Blue 28). 0.3 g of the dye are dissolved in 50 ml of ethanol,

diluted with 100 ml of water, and acidified with 5 ml of conc.  $\text{H}_2\text{SO}_4$ . After heating at  $50^\circ$ , 25 ml of 0.1 N  $\text{VSO}_4$  are added, and after 1 min the solution is cooled and titrated with 0.1 N  $(\text{NH}_4)_2\text{SO}_4 \cdot \text{Fe}_2(\text{SO}_4)_3$ , either potentiometrically or using safranin T (C. I. Basic Red 2) as indicator.

[Gio.Ser.]

**544 – Acidity constant of a protein conjugate in  $\text{D}_2\text{O}$**  (in English). W. Y. Wen and I. M. Klotz (Department of Chemistry, Northwestern University, Evanston, Ill., U.S.A.). *J. Phys. Chem.*, 65 (1961) 1085–1086.

The  $\text{pK}_a$  of dimethylaminoaphthalene-sulfonyl chloride, bound separately to protein and to a small reference molecule, was examined in  $\text{D}_2\text{O}$  and  $\text{H}_2\text{O}$ , respectively. No significant difference was detected, and therefore it was concluded that differences between hydrogen-bonding strengths in liquid water *vs.* hydration water of proteins are not appreciably different in  $\text{D}_2\text{O}$  as compared to  $\text{H}_2\text{O}$ .

[D.S.Ru.]

**545 – The effect of rennet on casein. Application of a titrimetric method at constant pH** (in French). J. Garnier, G. Mocquot and Mme G. Brignon (Station centrale de microbiologie et recherches laitières I.N.R.A., Jouy-en-Josas, Seine et Oise, France). *Compt. rend.*, 254 (1962) 372–374.

Les auteurs étudient l'action de la présure sur des solutions de caséine  $\alpha$  en milieu  $\text{NaCl}$  0.1 M à pH 6.95. Le pH, déterminé par potentiométrie à l'électrode de verre est maintenu constant ( $\pm 0.002$  unité de pH) par addition de soude. Dans les conditions précédentes, la quantité d'ions  $\text{H}^+$  libérée par la protéolyse est de  $1.8 \pm 0.35 \cdot 10^{-5}$  mole de  $\text{H}^+$  par g de caséine. Les auteurs envisagent l'hypothèse d'une coupure, par la présure, d'une liaison ester de la caséine entraînant l'apparition d'un groupe carboxylique dont le  $\text{pK}$  serait voisin de 4.

[Bad.Lam.]

See also abstracts nos. 459, 464, 477, 489.

## 5. Conductometry

**546 – Conductometric titration of weak inorganic acids and ammonium salts in aqueous media** (in English). F. Gaslini and L. Z. Nahum (Cartiera Vita Mayer and Co., Research Division, Milan, Italy). *J. Electroanal. Chem.*, 3 (1962) 85–89.

For the determination of weak inorganic mono- and polybasic acids, having  $\text{pK}$  values down to 12.5 and of their anhydrides and of ammonium salts, a conductometric method is proposed, which consists of titrating the sample, dissolved in an excess of aqueous ammonia, with alkali. The method is also applied to the determination of acids whose titration is difficult on account of their poor solubility or abnormal behaviour in water.

[Authors]

**547 – Electrolytic conductivity of lithium chloride, magnesium bromide and zinc chloride in water-tetrahydrofuran mixtures and in pure tetrahydrofuran** (in German). W. Strohmeier, A. El-said Mahgoub and F. Gernert (Institut für physikalische Chemie, Universität Würzburg, Deutschland). *Z. Elektrochem.*, 65 (1961) 85–91.

Die elektrolytische Leitfähigkeit von  $\text{LiCl}$ ,  $\text{MgBr}_2$  und  $\text{ZnCl}_2$  wurde in Abhängigkeit von der Konzentration in Wasser, Tetrahydrofuran und deren Gemischen über den ganzen Molenbruch gemessen. Die DK (Dielektrizitäts-Konstante) nahm von Wasser bis zu reinem THF von 80.4 bis 7.35 ab. Die Salze waren gut löslich. Bei DK-Werten  $> 39$  erweisen sich die Salze als starke Elektrolyte und dissoziieren bei kleinen Konzentrationen vollständig, die 1–2-wertigen in beiden Stufen. Bei DK-Werten  $< 39$  tritt keine vollständige Dissoziation mehr ein,  $\text{ZnCl}_2$  und  $\text{MgBr}_2$  dissoziieren nur noch wie 1–1-wertige Elektrolyte. Daneben können auch Ionen-Assoziate gebildet werden. Die Walden'sche Regel, die nur für Ionen mit grossen Radien gilt, trifft hier nicht zu, der Quotient  $(\Lambda_0/\eta)(\Lambda_0/\eta)_{\text{H}_2\text{O}}$  nimmt nach kleinen DK hin stark ab. Die Dissoziations-Konstanten  $K_1$  und  $K_3$  konnten berechnet werden. Bei  $\text{DK} = 11$  sind  $\text{LiCl}$  und  $\text{MgBr}_2$  gleich stark,  $\text{ZnCl}_2$  schwächer dissoziiert, ebenso wie bei metallorganischen Verbindungen, über die die Autoren eine weitere Veröffentlichung ankündigen. In reinem THF liegt das Leitfähigkeitsminimum bei höheren Konzen-

trationen als in den Mischlösungsmitteln, woraus auf die Bildung von Tripleionen  $M_2X_3^+$  und  $MX_3^-$  geschlossen werden kann. Eine Tabelle gibt die berechneten Ladungsabstände von Ionenpaaren und Tripleionen an. [He.We.]

**548 – Research on solvate formation in the system Mg halide–dimethylformamide–water** (in German). *J. prakt. Chem.*, 12 (1961) 198–205.

By means of conductivity measurements, it was possible to demonstrate the existence of a series of solvates (some of which were also isolated) between  $MgCl_2$  or  $MgBr_2$  and dimethylformamide (DMF), e.g.  $MgCl_2 \cdot 6DMF$ ,  $MgBr_2 \cdot 6DMF$ ,  $MgCl_2 \cdot 3DMF$ ,  $MgCl_2 \cdot 4DMF \cdot 2H_2O$ ,  $MgCl_2 \cdot 3DMF \cdot 3H_2O$  and  $MgCl_2 \cdot 2DMF \cdot 4H_2O$ . For the dissociation constant of  $MgCl_2$  in DMF the value  $2 \cdot 10^{-2}$  was found experimentally. [Ca.Cas.]

**549 – Structure of molten Hg halogenides** (in English). G. J. Janz and J. D. E. McIntyre (Rensselaer Polytechnic Institute, Department of Chemistry, Troy, N. Y., U.S.A.). *Ann. N. Y. Acad. Sci.*, 79 (1960) 790–802.

From experimental measurements of specific conductivity of molten  $HgBr_2$  in the range 240–320°, mol. and red. conductivities were calculated with the aid of published data on density and viscosity. The activation energies of electric conductivity and of viscous motion lie in the range 6.2–5.1 kcal/mol.; the activation energy for electric conductivity is a direct function of the temperature. [Ca.Cas.]

**550 – Use of methylglucamine standard solution for the determination of acids by high-frequency end-point indication** (in German). L. Balasz and E. Pungor (Laboratory for Inorganic and Analytical Chemistry, L. Eötvös University, Budapest, Hungary). *Mikrochim. Acta*, (1962) 309–313.

Methylglucamine (1-desoxy-1-methylamino sorbitol,  $C_7H_{17}O_5N$ ) is proposed as a titersubstance for the determination of acids in water. The real, solid base is very soluble and its dissociation constant is  $1.5 \cdot 10^{-5}$  at 22°. It has the advantage over ammonium hydroxide that standard solutions can be prepared by weighing the non-hygroscopic compound. The normality of the solution stored in a polyethylene bottle for three months changed about 1.5%. Titration curves obtained with a h.f. titrimeter for the determination of hydrochloric acid, acetic acid and oxalic acid are given. [F.Vor.]

**551 – The conductances of a number of acids and divalent metal salts in anhydrous ethanolamine** (in English). P. W. Brewster, F. C. Schmidt and W. B. Schaap (Department of Chemistry, Indiana University, Bloomington, Ind., U.S.A.). *J. Phys. Chem.*, 65 (1961) 990–992.

Conductance measurements were made of solutions of three halogen acids, benzoic acids and some salts of strontium, barium and lead in anhydrous ethanolamine. In dilute solutions the preeograms have positive slopes in the case of the acids and the lead salts. Suppression of solvent ionization and complex ion formation are suggested explanations in these cases. [D.S.Ru.]

**552 – Acetic anhydride as a non-aqueous ionising solvent. II. Conductometric and preparative studies in acetic acid-free acetic anhydride** (in German). G. Jander and H. Surawski (Anorganisch-Chemisches Institut der Technischen Universität, Berlin, Deutschland). *Z. Elektrochem.*, 65 (1961) 469–475.

Reinstes Essigsäureanhydrid unterliegt einer teilweisen Eigendissoziation nach der Gleichung:



Daher kann man gelöste Verbindungen, sofern sie die Konzentration der lösungsmittelleigenen Ionen erhöhen, als Säuren- bzw. Basenanalogue bezeichnen. Ein besonders stark dissoziierendes Säuren-analoges ist nach Messungen der Autoren Acetylperchlorat. Es wurden neutralisations-analoge Reaktionen, z.B. die von Acetylperchlorat mit einem starken Basenanalogen (Kaliumacetat), ebenso mit einem schwachen (Thalliumacetat) konduktometrisch verfolgt und die Entstehung von Metallperchloraten präparativ-analytisch nachgewiesen. Die Bindungsverhältnisse des Acetyliums werden diskutiert. Eine Umwandlung des Carbeniumions  $[CH_3-C^+ = O]$  in ein stabileres Carboxoniumion  $[CH_3-C^+ = O^+]$  wird vermutet. Die Solvation und Entstehung eines Acetyliums  $[(CH_3CO)_3O]^+$  wird angenommen und als Erklärungsmöglichkeit für die orange bis blutrote Färbung der Acetylperchloratlösungen erörtert. Die Ionisationsmöglichkeiten von  $SbCl_5$  und anderen Verbindungen in Essigsäureanhydrid werden diskutiert. Diese Verbindungen

zeigen partielle Solvolyse. Es wird nachgewiesen, dass die Existenz von Ansolvosäuren nicht möglich ist. (See also abstract no. 540). [He.We.]

**553 - Conductivity method for determination of urea** (in English). Wei-Tsung Chin and Wybe Kroontje (Agronomy Department, Virginia Agricultural Experimental Station, Virginia Polytechnic Institute, Blacksburg, Va., U.S.A.). *Anal. Chem.*, 33 (1961) 1757-1760. A new conductivity method for the determination of urea is given, which is based on the variations in the electric conductivity observed when ammonium carbonate is produced from urea by a solution of urease. High recovery and precision are obtained. The method is simple and rapid (100 urea determinations within 4-5 hours) and can be applied to a range of urea concentrations from 0.1-2000 p.p.m. Substances that interfere with urease activity must be excluded from the reaction. [Su.Mo.Ce.]

See also abstracts nos. 467, 475, 484, 490.

## 6. Electrolysis

**554 - Effect of temperature on the electrodeposition of cadmium from sulfate solutions** (in Russian). G. A. Emelyanenko and T. T. Got'manova (State University, Dnepropetrovsk, U.S.S.R.). *Zhur. iz. Khim.*, 36 (1962) 508-512.

The effect of temperature on the polarization and the rate of electrodeposition of cadmium from cadmium sulfate solutions were investigated. It was found that cathodic polarization is lowered with increasing temperature, and is accompanied by a decrease of the temperature coefficient of polarization in the region of 40-50°. The relation  $\log i - 1/T$  has an inflexion point in this region. Curvature of the  $\log i - 1/T$  curve toward the  $1/T$  axis is assumed to be due to the decreased contribution of electrochemical polarization and increased contribution of concentration polarization in the overall polarization of the electrode. [Ot.So.]

**555 - Potentiometric study and kinetic intensity of the effect of the  $Zn^{2+}$  ion on the electrodeposition of cobalt** (in French). J. Mindowicz, Mme C. Capel-Boute et C. Decroly (Université Libre de Bruxelles, Laboratoire de Métallurgie et Electrochimie, Belgique). *Compt. rend.*, 254 (1962) 1414-1416.

Par le tracé des courbes intensité-tension électrique relatives à la réduction sur cathode d'or de l'ion  $Co^{2+}$  (tracé potentiocinétique à la vitesse de 40 mV/min et tracé intensiocinétique à la vitesse de 4 mA/min) les auteurs mettent en évidence l'inhibition du dépôt de cobalt métallique par la présence d'ions  $Zn^{2+}$ . L'hypothèse précédemment admise d'un dépôt d'hydroxyde de zinc gênant l'approche et la décharge des ions  $Co^{2+}$  reste valable. L'influence de la température (entre 20 et 60°) et de la concentration des ions  $Zn^{2+}$  sur cette inhibition a été également étudiée. [An.Sn.]

See also abstract no. 488.

## 7. Coulometry

**556 - Coulometric determination of gold at controlled electric tension** (in English). J. E. Harrar and F. B. Stephens (University of California, Lawrence Radiation Laboratory, Livermore, Calif., U.S.A.). *J. Electroanal. Chem.*, 3 (1962) 112-116.

A rapid procedure for coulometric determination of gold at controlled electric tension in the mg

range was developed. It is based on electrodeposition of the gold from a 0.5 M HCl solution at an electric tension of +0.48 V *vs.* S.C.E. Background corrections are negligible and oxygen does not interfere. Only Ir(IV), Ru(IV), Ag and V(V) cause serious interference. [Authors]

**557 – Analysis of thallium amalgams** (in English). W. T. Foley and J. M. Osyany (Chemistry Department, St. Francis Xavier University, Antigonish, Nova Scotia, Canada). *Anal. Chem.*, 33 (1961) 1657–1658.

A method is described for determining thallium in thallium amalgams. A nitric solution of the amalgam is treated with sulfuric acid to obtain the sulfate, and with formic acid to precipitate the mercury. Final titration of thallium can be carried out either by a macro-iodometric method or, for microsamples, by a coulometric method using electrogenerated bromine as titrant solution. Results are reported for both types of titration. A method for the electrolytic purification of thallium sulfate is also given. [Su.Mo.Ce.]

**558 – Coulometric titration of antimony at controlled electric tension** (in English). L. B. Dunlap and W. D. Shults (Analytical Chemistry Division, Oak Ridge National Laboratory, Oak Ridge, Tenn., U.S.A.). *Anal. Chem.*, 34 (1962) 499.

Sb(III) can be detected by reduction at controlled electric tension at  $-0.28$  V *vs.* the S.C.E. at a mercury cathode. The reduction leads to metallic Sb in one step. The supporting electrolyte consists of 0.4 M  $\text{H}_2\text{C}_4\text{H}_4\text{O}_6$  and 1 M hydrochloric acid. Even Sb(V) can be reduced quantitatively at the mercury cathode, but only in a supporting electrolyte of about 6 M hydrochloric acid at  $-0.21$  V *vs.* the S.C.E. In this electrolyte the reduction leads first to Sb(III) and then at  $-0.35$  V to Sb(0). The current efficiency is almost 100%. Details of the procedure and some results are given. At the 5 mg level Sb(III) and Sb(V) can be detected with a relative error of 0.5%. Interference can be eliminated easily. [Kl.Gr.]

**559 – Electrogeneration of bromine by a pulse technique for coulometric titrations** (in English). Q. Fernando, M. A. V. Devanathan, J. C. Rasiah, J. A. Calpin and K. Nakulesparan (Department of Chemistry, University of Pittsburgh, Pa., U.S.A.). *J. Electroanal. Chem.*, 3 (1962) 46–53.

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

See also abstracts nos. 473, 474, 485.

## 8. Electrophoresis

**560 – Electrophoresis in starch gel** (in Czech). Č. Altaner (Oncological Research Institute, Bratislava, Czechoslovakia). *Chem. listy*, 56 (1962) 334–354.

A review of the technique of electrophoresis in starch gel is given, describing the procedure, apparatus, preparation of the gel and buffers employed, and also procedures for the detection of serum proteins, lipoproteins, haemoglobin, enzymes, ceruloplasmins and radioactive substances. Attention is also paid to methods of immunoelectrophoresis, bidimensional electrophoresis and preparatory methods. The second part of the review deals with practical applications. An exhaustive bibliography is included, extending to mid-1961. [Ot.So.]

**561 – Analysis of electrophoresis patterns: a comparison of two methods with the aid of Rayleigh interference optics** (in English). C. C. Curtain (Baker Medical Research Institute, Alfred Hospital, Melbourne, Victoria, Australia). *Australian J. Exp. Biol. Med. Sci.*, 39 (1961) 197–202.

Serum electrophoresis patterns can be resolved using the methods of Tiselius and Kabat, and of

Svedberg and Pedersen, by using a photo-electric Rayleigh fringe comparator. The plate holder of the Perkin Elmer model 38A instrument must be modified for the first method. Details of the modification are given. A comparison of the two methods is made and it is shown that the second one is less convenient, since the entire gradient curve must be plotted. [Gio.Ser.]

**562 – Paper electrophoresis of inorganic cations in the presence of complexing agents. II** (in French). P. E. Wenger, I. Kapétanidis and W. von Janstein (Laboratories of Mineral, Analytical and Micro-Chemistry, University of Geneva, Switzerland). *Mikrochim. Acta*, (1962) 184–193.

The authors studied the electrophoresis of Cd, Cu(II), Bi, As(III), Sb(III), Sn(II), Fe(III), Al, Cr(III), Ni, Co(II), Mn(II) and Zn in buffered solutions, containing  $\beta$ ,  $\beta'$ -diamino-diethylether, N,N'-tetraacetic acid. The pH range was 2–12. A theoretical explanation of the observed data cannot be given. Results are given in numerous tables and diagrams. Potentialities for separating the elements exist. [H.L.Ki.]

**563 – Determination of urinary 4-hydroxy-3-methoxymandelic acid by paper electrophoresis** (in English). D. Klein and J. M. Chernaik (Long Island Laboratories Inc., Flushing, N.Y., U.S.A.). *Clin. Chem.*, 7 (1961) 257–264.

The pH of a 3 ml sample of urine is adjusted to 2 with 3 N HCl and the sample is diluted to 24 ml with water. Three 2 ml samples are placed in stoppered tubes and heated for 10 min in boiling water. After cooling, the pH is adjusted to 0.5–1 with 3 N HCl and the tubes are extracted with three portions of ethyl acetate of 4, 2 and 2 ml. The combined extracts are evaporated and the residue is dissolved in ethanol. The ethanolic solution is applied to a Whatmann No.3 MM paper strip (3 cm  $\times$  30 cm). A standard solution of 4-hydroxy-3-methoxymandelic acid is also applied on the same paper strip. The electrophoresis is carried out overnight at 4 mA in 0.5% acetic acid. After drying the strip, both sides are sprayed with a diazo reagent obtained by mixing 10 ml of 0.1% *p*-nitroaniline in 2% HCl with 10 ml of 0.2% NaNO<sub>2</sub> and 10 ml of 10% K<sub>2</sub>CO<sub>3</sub>. The compound appears as a purple band which migrates towards the anode. The band is cut and eluted with alkaline methanol (50 ml of methanol mixed with 25 ml of 2% Na<sub>2</sub>CO<sub>3</sub>). A blank is obtained from an unstained part of the strip. The colour is read in a colorimeter at 520 m $\mu$ . The values found were between 1.1 and 3.9  $\mu$ g/mg of creatin, which means an excretion of around 1.2 to 3.7  $\mu$ g per min. [Gio.Ser.]

**564 – Determination of histamine and histidine by high voltage paper electrophoresis** (in Czech). M. Ferenčík (Veterinary Centre, Bratislava, Czechoslovakia). *Chem. listy*, 56 (1962) 289–291.

A simple, rapid and accurate method is described, which is also suitable for routine analysis when combined with photometric evaluation of the electrophoreograms. A pyridine-acetic acid buffer of pH 3–5 is used. Concentrations of the individual components in the experiments were 0.01–0.05 M, ionic strength was about 0.01, gradients were up to 70 V/cm, and electrophoresis times were 20–30 min. After detection by Pauly's reagent the spots were cut out and eluted, and the solutions were evaluated photometrically. [Ot.So.]

**565 – Quantitative determination of diaminocarboxylic acids and related compounds by rapid paper electrophoresis** (in English). Mary A. Doran (Eastern Research Laboratory, The Dow Chemical Co., Framingham, Mass., U.S.A.). *Anal. Chem.*, 33 (1961) 1752–1755.

Intermediate products formed during the carboxymethylation of ethylenediamine, for the production of EDTA, have been studied. Rapid analytical procedures for the simultaneous determination of aminocarboxylic acids and related compounds are described. The compounds are complexed with cupric ion, and cupric complexes of EDTA, N,N-ethylenediglycine, N,N'-ethylenediglycine and nitrilotriacetic acid are separated by low electric tension paper electrophoresis. Estimation is made spectrophotometrically after color development of the bands with sodium diethyldithiocarbamate, with a precision of  $\pm 2.5\%$ . Paper electrophoresis and ninhydrin development is used for the quantitative evaluation of the following, with a precision of  $\pm 5\%$ ; N,N-ethylenediglycine, N,N'-ethylenediglycine, N-(2-aminoethyl)glycine, 2-oxo-1-piperazineacetic acid, 2-oxo-piperazine, iminodiacetic acid, glycine and ethylenediamine. [Su.Mo.Ce.]

**566 – Electrophoretic separation of proteins on emulsions of adsorbents** (in English). W. Ostrowski (Department of Physiological Chemistry, Academy of Medicine, Krakow, Poland). *Clin. Chim. Acta*, 6 (1961) 38–43.

The electrophoretic separation of proteins can be achieved by electrophoresis on an immobilised medium, which is obtained by using various adsorbents emulsified in a buffer solution containing



0.2% agar. Starch, cellulose powder, Celite 535, titanium dioxide, and Hyflo-supercell were tested. Hyflo-supercell in concentrations of 1–5% gave the best results. [Gio.Ser.]

**567 – Dye binding by protein as applied to quantitative paper electrophoresis** (in English). D. A. Osborn (Institute of Laryngology and Otology, University of London, Great Britain). *Clin. Chim. Acta*, 5 (1961) 777–794.

The binding of different dyes was studied. It is shown that the binding varies according to the treatment: the nature of the dye solvent, the method of denaturation, the temperature and the duration of washing are all involved. The binding of light green (C. I. Acid green 5) is not linear with concentration. A comparison is made of the behaviour of the latter with that of lissamine green (C. I. Acid green 4) and bromocresol green. [Gio.Ser.]

**568 – Electrophoresis of casein in a column stabilised by a density gradient** (in English). W. Manson (The Hannah Dairy Research Institute, Ayr, Scotland). *J. Electroanal. Chem.*, 3 (1962) 203–208.

The application of zonal electrophoresis in a column stabilised by a density gradient to casein is described. In general, the procedure yielded results similar to those obtained by moving boundary electrophoresis, and separated certain of the components of the casein complex in quantities sufficient for further study. [Author]

**569 – Electrophoretic study of serum albumin** (in French). N. Benhamou, M. Baruch, J. Guastalla and S. De Mende (Laboratoire de chimie physique de la Faculté des Sciences de Paris, et Centre d'Electrophorèse du C.N.R.S., France). *J. chim. phys.*, 59 (1962) 289–298. The authors determined separately the electrophoretic mobility of quartz particles in suspension in solutions of bovine serum albumin, and the mobility of the same protein in solution at the same pH value.

In acetate buffer, the electrophoretic mobility of quartz particles is negative, but for the same value of pH it becomes positive in the presence of serum albumin. The mobility increases with increasing concentration of serum albumin and remains constant over a large range of concentrations. The extent of this range depends on the value of pH, and corresponds to particles of quartz completely covered by molecules of serum albumin. The electrophoretic mobility then decreases at higher concentrations. The study of electrophoretic mobility of serum albumin by the methods of Kern and Tiselius indicates the existence of a slow form. The proportion of this form increases with concentration, and this would explain the reduction in mobility of the quartz at high concentrations of serum albumin. [G.Mar.]

**570 – Electrophoretic sub-fractionation of human serum lipoproteins using TEB buffer.** (in English). F. R. Sonnino and P. P. Gazzaniga (Institute of General Pathology, University of Rome, Italy). *Clin. Chim. Acta*, 6 (1961) 295–297.

A method is proposed for obtaining better separation and sharper resolution in the electrophoretic analysis of serum lipoproteins. The method is based on the use of a buffer consisting of 0.5 M tri-(hydroxymethyl)methylamine, 0.02 M EDTA and 0.07 M boric acid. The pH of the recommended buffer is 8.8, with an ionic strength of 0.5. [Gio.Ser.]

**571 – Detection of coeruloplasmin after zone electrophoresis** (in English). J. A. Owen and H. Smith (St. Vincent Hospital, Melbourne, Australia). *Clin. Chim. Acta*, 6 (1961) 441–444.

A stain was described previously to detect haemoglobin and its complexes with haptoglobins. The method has been modified to increase the sensitivity, thus showing a reactive zone after gel electrophoresis, which is independent of the haptoglobin complexes, and which has been identified as coeruloplasmin. The stain is made by mixing 1% *o*-dianisidine solution in water (HCl is added in an amount just sufficient to complete the dissolution) with acetate buffer (pH 5.7), 95% ethanol and water, in the proportions 1 : 1 : 3 : 5. Zone electrophoresis is carried out at pH 6.5, after which the strip is immersed in the reagent for 2 h at 37° and washed. The coeruloplasmin gives a pink stain on paper and an orange–red one on starch gel. [Gio.Ser.]

**572 – Quantitative electrophoresis of serum proteins in the presence of haemoglobin** (in English). C. C. Curtain (Baker Medical Research Institute, Alfred Hospital, Melbourne, Australia). *Australian J. Exp. Biol. Med. Sci.*, 39 (1961) 203–208.

The presence of haemoglobin interferes with the electrophoresis patterns of serum. To calculate the amount of haemoglobin in the electrophoretic cell, after the pattern has been photographed as usual, an image of the cell is taken directly, after the cylindrical lens of the optical system has been removed, in green light of 546  $\mu$ . From this picture the distribution of haemoglobin in the cell is determined by densitometry. Two inflexions in the densitometric curve are present: the first is due to free haemoglobin, and the second is due to the haptoglobin–haemoglobin complex. The

assumption is made that free and bound haemoglobin have the same extinction coefficient at 546 m $\mu$ . [Gio.Ser.]

**573 – Electrophoretic research on aged human blood haemoglobin and maceration of human blood stains** (in French). M. Muller, G. Fontaine, P. H. Muller and A. Gourguechon (Institut de Médecine Légale, Laboratoire d'Immunochimie, Lille, France). *Rev. franç. clin. biol.*, 6 (1961) 177–181.

Electrophoretic migration on paper for haemoglobin coming from two years old blood stains is higher than that of haemoglobin coming from blood kept at 4° for the same period, which, in turn, has a mobility greater than a fresh sample; on agar the reverse sequence was found. These differences are attributed to chemical changes. [Ca.Cas.]

**574 – Separation of human haemoglobins by starch gel electrophoresis** (in English). R. L. Engle Jr., A. Markey, J. H. Pert and K. R. Woods (Department of Medicine, New York Hospital, Cornell Medical Centre, N. Y., U.S.A.). *Clin. Chim. Acta*, 6 (1961) 136–141.

A method is described for separating normal and abnormal haemoglobins, with very little tailing. Haemoglobin A<sub>2</sub> is easily separated, and so are two other pigmented and two non-pigmented fractions in normal red cell haemolysates. Foetal haemoglobin can easily be distinguished from haemoglobin A, when both are present, by this method. [Gio.Ser.]

**575 – Studies on the analysis of steroid hormones by high-voltage paper electrophoresis. IV. The electrophoretic patterns of the crude conjugated oestrogens in urine.** Toshio Iso (School of Medicine, Tokyo Medical and Dental University, Tokyo, Japan). *J. Japan. Biochem. Soc.*, 31 (1961) 449–452.

The urine of pregnant females was extracted with butanol to yield a crude solution of conjugated oestrogens. The solutions was subjected to electrophoresis on filter paper in formic acid–acetic acid at 40 kV. Eight conjugated oestrogen fractions could be detected by fluorescence under u.v. light, followed by assay of the oestrogenic activity. [Gio.Ser.]

See also abstracts nos. 462, 471, 472.

## 9. Other methods

**576 – Electrochemical indicators** (in French). G. Charlot and B. Trémillon (Laboratoire de chimie analytique, 10, rue Vauelin, Paris, France). *J. Electroanal. Chem.*, 3 (1962) 1–23. A review concerning the application of electrochemical indicators in various fields of electrochemical analysis. This review is completed with a table containing the various indicators: polarographic, amperometric, chronopotentiometric and potentiometric, and gives many examples of possible titrations. [Red.]

**577 – Chronopotentiometry with programmed current. II. Response function additivity principles applied to current programming and multicomponent systems** (in English). R. W. Murray and C. N. Reilley (Department of Chemistry, University of North Carolina, Chapel Hill, N.C., U.S.A.). *J. Electroanal. Chem.*, 3 (1962) 182–202.

The principle of additivity of response functions forms the basis of a new method for derivation of theoretical chronopotentiometric transition time relations for programmed currents and multicomponent systems with diffusion-controlled transport. To use the method it is necessary to have available, for all types of single current impulses used, the characteristic current impulse response functions describing the diffusion gradients and surface depletions for single component systems. These are obtained through solution of Fick's law. Response function additivity is utilized in multicomponent systems by summing the *n*- and *D*-weighted surface depletions of all reactants; the resulting surface concentration response function is then at all times equal to the impulse current response function characteristic of the current impulse used for linear diffusion. In current

programming, the  $n$ - and  $D$ -weighted surface depletion of the electroactive species is, by the response additivity principle for linear diffusion, equal to the summation of the response functions of all current impulses employed, each current impulse response function being written for the time of usage of the respective current impulse. Solutions of Fick's law to obtain the chronopotentiometric transition time relations for such cases is therefore unnecessary. Generalized relations are given for multi-component systems and current programming, and for combinations of the two cases. The method of derivation is illustrated using a number of known cases. New equations are derived for the specific cases of (1) single component systems: step-reverse-ramp, step-reverse-square root of time, step-plus-negative ramp and ramp-reverse-ramp current reversal programs, step-wise reactions with any power of time current impulse, square root of time impulse program, staircase, square-wave, and sawtooth periodic current programs (linear diffusion), and multi-step and step-reverse-step current programs (spherical and cylindrical diffusion), (2) multicomponent systems: step and square root of time current impulses (spherical and cylindrical diffusion).

[Authors]

**578 – Chronopotentiometry in acetic anhydride. Oxidation and reduction of the solvent** (in English). W. B. Mather Jr. and F. C. Anson (Gates and Crellin Laboratories of Chemistry, California Institute of Technology, Pasadena, Calif., U.S.A.). *Anal. Chem.*, 33 (1961) 1634–1637.

Chronopotentiometric studies were undertaken to elucidate the anodic and cathodic reactions that occur during the passage of current through solutions of sodium perchlorate in acetic anhydride–acetic acid solutions. Results obtained show why the coulometric generation of hydrogen ions at platinum anodes does not achieve a 100% current efficiency (maximum obtainable 95%). In fact, hydrogen and acetylum ions are formed at the platinum anode and the acetic anhydride condenses with the acetylum ions to form basic products that actually remove hydrogen ion from the solution. Cathodic reduction is not so complicated; hydrogen and acetate ion are formed at the cathode.

[Su.Mo.Ce.]

**579 – Chronopotentiometry with current programmed as a function of time** (in English). R. W. Murray and C. N. Reiley (Department of Chemistry, University of North Carolina, Chapel Hill, N.C., U.S.A.). *J. Electroanal. Chem.*, 3 (1962) 64–77.

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

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

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

[Authors]

**580 – The application of the galvanostatic electric tension–time technique to analysis in molten salts** (in English). D. Inman and J. O'M. Bockris (John Harrison Laboratory of Chemistry, Philadelphia, Pa., U.S.A.). *J. Electroanal. Chem.*, 3 (1962) 126–145.

Transition times of electrode processes have been determined from cathode electric tension–time relations at constant current, and at various concentrations, current densities and temperatures, in the following molten salt solutions:  $\text{PbCl}_2$  in  $\text{LiCl-KCl}$ ;  $\text{AgNO}_3$  in  $\text{NaNO}_3$ ;  $\text{AgNO}_3 + \text{NaCl}$  in  $\text{NaNO}_3$ ;  $\text{AgNO}_3$  in  $\text{NaNO}_3\text{-KNO}_3$ ;  $\text{AgNO}_3 + \text{KCN}$  in  $\text{NaNO}_3\text{-KNO}_3$ ;  $\text{Pb(NO}_3)_2$  in  $\text{NaNO}_3$ ;  $\text{PbCl}_2$  in  $\text{NaNO}_3\text{-KNO}_3$  and  $\text{Cd(NO}_3)_2$  in  $\text{NaNO}_3\text{-KNO}_3$ .

In general, Sand's equation for the transition time, in the case of mass transfer by semi-infinite linear diffusion, is obeyed. Diffusion coefficients, energies of activation for the diffusion processes and solubility products are calculated. Information concerning complex formation and the structure of molten salts is reported.

[Authors]

**581 – Microdetermination of molecular hydrogen by means of galvanometric analysis** (in English). P. Hersch (Arthur D. Little Research Institute, Inveresk, Midlothian, Scotland). *Proc. Intern. Symp. Microchem.*, (1959) 141–150.

The gas is carried by means of  $\text{N}_2$ , after mixing with  $\text{O}_2$  (whose concn. must be kept constant during the whole run) on to platinized  $\text{SiO}_2$ . The difference in the  $\text{O}_2$  content before and after the catalytic combustion is measured by means of an  $\text{O}_2$  sensitive galvanometric device (Ag, Pb and KOH) and gives the  $\text{H}_2$  concn. The method is particularly suitable for very low concentrations of  $\text{H}_2$ , such as those encountered in metal corrosion.

[Ca.Cas.]

**582 – Influence of pH and of the formation of complexes on the anodic oxidation of indium amalgam** (in French). Mme M. Breant et M. J.-C. Merlin (Laboratoire de chimie minérale, Faculté des Sciences de Lyon, France). *Compt. rend.*, 254 (1962) 665–667.

Les auteurs proposent une étude du pouvoir réducteur de l'amalgame d'indium en fonction du pH et des propriétés complexantes de la solution aqueuse en contact avec cet amalgame. La dissolution anodique de l'indium amalgamé, étudiée par chronoampérométrie linéaire, permet d'obtenir des courbes intensité-tension électrique bien définies dans tout le domaine de pH (0-14). La tension électrique de demi pic  $E_{1/2}$  permet de caractériser le pouvoir réducteur de l'amalgame. La valeur de  $E_{1/2}$  est  $-0.445 \pm 0.01$  V (E.C.S.) entre pH 0 et 5.5, puis elle décroît comme 0.08 pH pour atteindre  $-1.1$  V à pH 14. Il s'agirait d'une oxydation selon  $\text{In}(\text{Hg}) + 3\text{HO}^- - 3e \rightarrow \text{In}(\text{OH})_3 \downarrow$  qui serait lente (pente théorique  $-0.058$ , pente expérimentale  $-0.08$ ). Le système  $\text{In}(\text{Hg})/\text{In}^{3+}$  est également lent en milieu acide:  $E_{\frac{1}{2}\text{an}} - E_{\frac{1}{2}\text{cat}} > 0.5$  V. La présence d'un certain nombre d'anions facilite l'oxydation de l'indium. Parmi les onze milieux étudiés citons l'action complexante des tampons acétique, citrique, pyrophosphorique et phosphorique qui abaissent la tension électrique demi pic respectivement de 200, 200-300, et 235 mV. [An.Sn.]

**583 - The influence of the mobility of the  $\text{NH}_2$  group on the dielectric relaxation behaviour** (in German). H. Kramer (Physics Institute, The University, Mainz, Germany). *Z. Naturforsch.*, 15A (1960) 974-979.

Die elektrische Absorption von chlosubstituierten Anilinen zwischen 10.35 cm und 0.696 cm wurde in zwei Anteile aufgeteilt mit den Zuordnungen zur Beweglichkeit des Gesamtmoleküls und zu der Gruppe. Das Relaxationsverhalten wird nach der Budo'schen Theorie berechnet und der Substituenteneinfluss auf den Winkel zwischen  $\text{NH}_2$ -Moment und CN-Bindungsachse abgeschätzt. Zur weiteren Klärung dieses Einflusses sind Absorptionsmessungen bei kürzeren Wellenlängen nötig. [He.Be.]

**584 - Identification of nucleic acid components by a combined method of electro dialysis and circular paper chromatography** (in Russian). E. K. Alimova, G. D. Bolgova and A. T. Astvatsatur'yan (State Medical Institute, Rostov on Don, U.S.S.R.). *Biokhimiya*, 26 (1961) 221-224.

The nucleic acids are hydrolysed with 1 N  $\text{H}_2\text{SO}_4$  for 1 h at  $100^\circ$  and neutralised with  $\text{Ba}(\text{OH})_2$ . After centrifuging to remove  $\text{BaSO}_4$ , the volume is made up to 10 ml and the solution is electro dialysed at 100 V and 20-25 mA for 30 min. The purines migrate to the cathode fraction and the pyrimidine nucleotides to the anode, while the carbohydrates remain in the middle. The pyrimidine fraction is hydrolysed with  $\text{HClO}_3$  to yield the free bases and electro dialysed again. The different fractions obtained are evaporated to dryness, redissolved in a small volume and subjected to circular paper electrophoresis, together with suitable controls, in order to identify the different components. The chromatogram is developed with *n*-butanol-1 N  $\text{NH}_3$ (7 : 1) for the bases and with *n*-butanol-acetic acid-water (4 : 1 : 5) for the sugars. [Gio.Ser.]

See also abstracts nos. 468, 476.

## 10. Related topics

**585 - Use of a molten mixture of halogens as electrolyte in a combustion cell functioning at high temperatures** (in French). R. Barde, R. Buvet and J. Dubois (Direction des Etudes et Recherches d'Electricité de France, Centre d'essais de Fontenay, Clamart, Seine, France). *Compt. rend.*, 254 (1962) 1627-1629.

Le tracé des courbes intensité tensions électriques relatives à l'oxydation électrochimique de différents combustibles ( $\text{H}_2$ , CO,  $\text{C}_4\text{H}_{10}$ , hexane, éther de pétrole, carbone) et à la réduction de l'oxygène, permet de prévoir le fonctionnement de différentes piles à combustibles. L'étude électrochimique a été réalisée à  $500^\circ$  dans un eutectique liquide LiCl-KCl, avec une électrode d'or. La réduction de l'oxygène semble résulter d'une réaction dont le siège serait la ligne de triple contact: combustible gazeux, électrode solide, électrolyte liquide. Les courants d'oxydation observés sont faibles sauf dans le cas de l'hydrogène. Les auteurs fournissent la courbe caractéristique de

décharge d'une pile hydrogène-oxygène élémentaire en milieu LiCl-KCl fondu à 500°: la tension disponible à courant nul est supérieure à 1 V et devient nulle pour des courants de 0.75 mA/cm. [An.Sn.]

**586 - Inhibition of hydrogen ion reduction at a platinum electrode by tin hydrous oxide film formation** (in English). A. J. Bard (Harvard University, Cambridge, Mass., U.S.A.). *J. Electroanal. Chem.*, 3 (1962) 117-125.

Evidence is presented for inhibition of hydrogen ion reduction in acidic halide media at a platinum electrode in the presence of tin. This inhibition is traced to a film of tin hydrous oxide formed when hydrogen ion is reduced, causing the pH to increase in the vicinity of the electrode, and allowing hydrolytic precipitation to occur. The film was investigated employing voltammetry, chronopotentiometry and spectrophotometry. The stability of the film and its effect on other electrode reactions was examined, and a mechanism for its formation proposed. [Author]

**587 - The influence of anions and time after activation on the heat of adsorption of hydrogen on platinum electrodes** (in German). M. Breiter and B. Kennel (Physikalisch-Chemisches und Elektrochemisches Institut der Technischen Hochschule, München, Deutschland). *Z. Elektrochem.*, 64 (1960) 1180-1187.

Die Adsorption von Wasserstoff an glatten Platin-Elektroden in Elektrolytlösungen wurde bei 0 bis 70° untersucht und anhand von Stromdichte-Spannungs-Kurven gezeigt, dass die Anionen einen Einfluss auf die Adsorptionswärme ausüben. Aus den  $i-U$ -Kurven wurden die Adsorptionsisothermen durch Integration erhalten. Es wurde die potentiostatische Dreiecksmethode (Will und Knorr, *Z. Elektrochem.*, 64 (1960) 258-269) benutzt. Als Elektrolyten dienten  $HClO_4$  und  $NaOH$  sowie  $HCl$  und  $HBr$  verschiedener Konzentration. In einem zweiten Teil wird über Untersuchungen des Oberflächenzustandes der Platin-Elektrode in 2.3  $M$   $H_2SO_4$  in den ersten 20 Minuten nach einer anodischen Polarisation bei Temperaturen von -10° bis +90° berichtet. Die zeitliche Abnahme der Wasserstoffadsorption geht bei allen Temperaturen annähernd gleichartig vor sich und wird mit einer Abnahme der Oberflächenrauigkeit erklärt. [He.We.]

**588 - Investigation of the formation and decomposition of hydrogen and oxygen films on platinum by a new instantaneous method** (in German). F. G. Will and C. A. Knorr (Physikalisch-Chemisches und Elektrochemisches Institut der Technischen Hochschule, München, Deutschland). *Z. Elektrochem.*, 64 (1960) 258-269.

Die Autoren beschreiben eine elektrodenkinetische Mess-Methode, mit deren Hilfe man Adsorptionserscheinungen an Edelmetall-Oberflächen untersuchen kann. Es wird zwischen der Versuchselektrode und einer praktischen stromlosen Wasserstoffnormalelektrode als Bezugsselektrode eine periodische, proportional der Zeit zu- und wieder abnehmende sogenannte Dreiecksspannung mit Hilfe eines elektronischen Potentiostaten angelegt. Die Periode ist über mehrere Größenordnungen variabel. Amplitude und Frequenz sind veränderlich. Der von der Dreiecksspannung abhängige Zellenstrom zwischen Versuchselektrode und Gegenelektrode wird oszillographisch verfolgt. Die Adsorption von Sauerstoff und Wasserstoff an Platin, der Auf- und Abbau von Schichten und die hierbei wirkenden Reaktionshemmungen sind mit dieser Methode untersucht worden. Die Autoren stellten fest, dass bei anodischer Vorbehandlung der Elektrode eine vorübergehende Aufrauung der Oberfläche verursacht wurde. [He.We.]

**589 - Kinetics of the electrochemical reaction between zinc amalgam and zinc sulphate solution** (in French). Mme. A. M. Baticle (Laboratoire d'Electrolyse du C.N.R.S., 1, Place Aristide-Briand, Bellevue, Seine et Oise, France). *Compt. rend.*, 254 (1962) 668-670.

Une étude théorique antérieure (A. M. Baticle et Y. Thouvenin, *Compt. rend.*, 248 (1959) 794) permet d'accéder aux paramètres cinétiques de la réaction,  $Zn(Hg) \rightleftharpoons Zn^{2+} + 2e$ , soit les grandeurs:  $k_s$  constante de vitesse de transfert,  $\alpha$  et  $(1-\alpha)$  coefficients de transfert anodique et cathodique. La mesure expérimentale consiste en la détermination de courants continus traversant l'électrode d'amalgame lorsque celle-ci est portée à des tensions électriques comprises dans l'intervalle  $E_{eq} \pm 2$  mV ( $E_{eq}$  tension électrique d'équilibre variant avec la composition de la solution, "0.005  $M$  <  $Zn^{2+}$  < 0.1  $M$ ", et celle de l'amalgame, "0.005% <  $Zn$  < 10%"; électrolyte indifférent  $Na_2SO_4$ , 0.5  $M$ ). Les résultats obtenus sont:  $k_s = 0.208 \cdot 10^{-2} \text{ cm}^{-1}$ ,  $\alpha = 0.69$  ( $1-\alpha$ ) = 0.30. Ces deux dernières valeurs sont en accord avec les résultats de Gerischer,  $\alpha = 0.72$ , et de Bodov et Lossev,  $\alpha = 0.70$ . [An.Sn.]

**590 - Oscillographic investigation of the electrode reaction in the system cadmium-aqueous solution by an intermittent galvanostatic measuring method** (in German). R. W. Ohse (Institut für physikalische Chemie der Universität Erlangen, Deutschland). *Z. Elektrochem.*, 64 (1960) 1171-1179.

Eine Cd-Elektrode wurde in wässriger Lösung über den gesamten pH-Bereich, hauptsächlich in alkalischer Lösung, mit einer periodischen Folge von Strom-Rechteckimpulsen anodisch und kathodisch belastet. Der zeitliche Verlauf der Bezugsspannung wurde mit einem Kathodenstrahl-Oszillographen gemessen und photographisch registriert. Dabei wurden zwei Spannungsniveaus bei anodischer Belastung mit bestimmten Stromdichten beobachtet, die unterhalb der Gleichgewichtsbezugsspannung der Sauerstoff-Elektrode lagen. Den gemessenen Ruhe-Bezugsspannungen liegen die Bildung von  $\text{Cd}(\text{OH})_2$  nach der Elektrodenreaktion,  $\text{Cd}^{2+} + 2 \text{OH}^- \rightarrow \text{Cd}(\text{OH})_2$ , und von CdO nach  $\text{Cd}^{2+} + \text{Cd}(\text{OH})_2 \rightarrow 2 \text{CdO} + 2 \text{H}^+$ , zugrunde. Es wurde nachgewiesen, dass zeitlich zuerst  $\text{Cd}(\text{OH})_2$  und dann CdO gebildet wurde. Dies wurde auch mit der durch Elektronenbeugungsaufnahmen und röntgenographischen Untersuchungen anderer Autoren nachgewiesenen örtlichen Schicht-Reihenfolge  $\text{Cd}-\text{CdO}-\text{CdO}(\text{OH})_2-\text{OH}$ -Lösung verglichen. Die Oszillogramme liessen auf die Bildung eines kurzlebigen (30 msec) und instabilen höheren Cadmiumoxydes sowie eines instabilen Cadmiumhydrides  $\text{CdH}_2$  schliessen. Im Zusammenhang damit wurde der Einfluss des Sauerstoffes und der Reaktionsmechanismus bei kathodischer Belastung diskutiert.

[He.We.]

**591 – Surface potential and surface tension of aqueous solutions of simple methylketones** (in Polish). B. Zapiór (Department of General Chemistry, Jagellonian University, Kraków, Poland). *Roczniki Chem.*, 36 (1962) 335–344.

Surface potential and surface tension of aqueous solutions of some ketones, dimethyl-, methyl-ethyl-, methylpropyl-, methylbutyl- and methylamylketone were measured. The parallelism in the electrocapillary properties of these substances was observed, and for surface potential an equation is given, which is analogous to the surface tension formula given by Szyszkowski.

[Ad.Hu.]

**See also abstract no. 531.**

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