Journal of

ELECTROANALYTICAL CHEMISTRY

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

ELSEVIER

GENERAL INFORMATION

REPORT FOR DISCUSSION AND COMMENT
ABBREVIATED REPORT OF THE "NOMENCLATURE AND ELECTROCHEMICAL DEFINITIONS" COMMITTEE OF C.I.T.C.E. AND OF THE "SYMBOLS AND ELECTROCHEMICAL TERMINOLOGY" SUB-COMMITTEE OF I.U.P.A.C.

This is an abbreviated version of the report already published in this Journal (2 (1961) 265–290 and 6 (1963) 173) and was prepared by G. MILAZZO and P. VAN RYSSELBERGHE. The translation into English was prepared by R. PARSONS and is presented here in order that a wider group of electrochemists and electro-analytical chemists may become aware of the direction in which Nomenclature discussions are taking. Comments direct to C.I.T.C.E. (Professor PIERRE VAN RYSSELBERGHE, Department of Chemistry, Stanford University, Stanford, California, U.S.A.) or (if in publishable form), to this Journal, will be welcome.

R. DEFAY, N. IBL, E. LEVART, G. MILAZZO, G. VALENSI AND P. VAN RYSSELBERGHE,

ELECTROCATALYSIS

The factors influencing the rate of electrochemical reactions have been discussed. Choice of the rational potential scale for comparison of the catalytic activity of electrodes is a prerequisite for the systematic development of the electrochemical catalysis. Electronic and surface properties of metals can be altered to enhance electrocatalysis. Examples of other ways of enhancing activity are given.

The mechanism of hydrocarbon oxidation is discussed in the example of ethylene. Discharge of water molecules is the rate determining step for olefin oxidation. Characteristic properties of noble metals for the ethylene oxidation are given. Oxide formation is an important limiting feature in hydrocarbon oxidation.

The mechanism of electrocatalysis is formulated for the hydrogen evolution and hydrocarbon oxidation reactions. For the h.e.r., the exchange current density depends on the d-character of the metal and the heat of adsorption of H. Criticism of this analysis are suggested.

Further study of the fundamentals of organic adsorption and electrode kinetic theory are required. Information of a large number of rationally chosen materials is necessary for a solid theory of catalysis.

J. O'M. BOCKRIS AND H. WROBLOWA,

ELECTROCHEMICAL KINETICS OF PARALLEL REACTIONS

The electrochemical oxidation of complex molecules (*e.g.*, hydrocarbons) sometimes involves branched reactions. Under these conditions, it is difficult to define a reversible potential and the coulombic efficiencies of product formation may then be potential-dependent.

A number of cases of the kinetics of branched reactions of the type $A \to B \overset{C}{\underset{D}{\diagdown}}$ with step $A \to B$ rate-determining, are worked out. It is found that in most cases, the coulombic yields are potential-dependent over certain potential regions. The calculated variation of coulombic yields with potential is compared with results obtained in the anodic oxidation of some unsaturated hydrocarbons.

E. GILEADI AND S. SRINIVASAN,

THE ELECTROCHEMICAL BEHAVIOR OF COPPER(II) AND COPPER(I) IONS IN A SERIES OF N,N-DIMETHYLALKYL-AMIDES AND N,N-DIALKYLACETAMIDES

The electrochemical behavior of copper ions has been investigated in N,N-dimethylformamide, N,N-dimethylacetamide, N,N-diethylacetamide, N,N-diisopropylacetamide, N,N-dibutylacetamide, N,N-dimethylpropionamide, N,N-dimethylbutyramide, and N,N-diisopropylpropionamide. The potentials of the two copper couples in these amides are in the normal order, and copper(I) solutions, as a result, are stable with respect to disproportionation. Except for the fact that the potentials of the copper(II)–copper(I) and copper(I)–copper(o) couples are slightly more negative than in the lower alcohols because of the slightly higher solvation energy of copper(II) and copper(I) ions in amides than in alcohols, the electrochemical behavior of copper ions in amides is very similar to that in the lower alcohols. Changes in the carbon-chain length of the alkyl group attached to the carbonyl carbon appear to have a greater effect on the solvation energy of copper(II) ion in amides than changes in the carbon-chain length of the alkyl groups attached to the nitrogen.

K. W. BOYER AND R. T. IWAMOTO,

A POTENTIOMETRIC STUDY OF THE REACTION BETWEEN V_2O_5 AND MOLTEN KNO_3

The reaction between V_2O_5 and molten KNO_3 is studied potentiometrically by conducting acid–base titration experiments *in situ*. An oxygen electrode is used as indicator electrode. The titration curves show three distinct potential drops. The first step is due to the transformation of V_2O_5 into metavanadate which reacts instantly with the nitrate base-electrolyte to yield pyrovanadate and a nitrate complex of the probable formula $[VO_3-O-NO_2]^{2-}$. Both compounds change upon neutralization into orthovanadate along the second and third steps, respectively, of the titration curves.

The effect of varying the temperature, fusion time, concentration of V_2O_5 and the effect of the addition of increasing quantities of $NaVO_3$ and $Na_4V_2O_7$ on the titration curves of V_2O_5–KNO_3 melts is investigated in detail. A mechanism accounting for the disappearance of the pentoxide is proposed. The reaction between V_2O_5 and molten KNO_3 is zero-order with respect to V_2O_5.

A. M. SHAMS EL DIN AND A. A. EL HOSARY,

Announcements

EIGHTH CONFERENCE ON ANALYTICAL CHEMISTRY
IN NUCLEAR TECHNOLOGY

The Eighth Conference on Analytical Chemistry in Nuclear Technology, on the *Determination of Interstitials and Trace Constituents in Reactor Materials and Products*, will be held in Gatlinburg, Tennessee, on October 6, 7 and 8, 1964, under the sponsorship of the Analytical Chemistry Division of the Oak Ridge National Laboratory. In addition of the technical sessions, an exhibition of modern analytical instruments and laboratory equipment will be held for the first time.

The Conference will be composed of six sessions embracing the following subjects:
1. Spectrochemical and X-Ray Methods of Analysis.
2. Mass Spectrometric Methods of Analysis.
3. Nuclear Methods of Analysis.
4. Gas Chromatographic Methods of Analysis.
5. Determination of Carbon, Hydrogen and Nitrogen in Metals.
6. Determination of Trace Constituents by Diverse Methods.

Participation in the conference will be on the basis of invited contributions; however, a limited number of papers, up to 25 minutes in length, are solicited and will be accepted provided the subject matter of such contributed material fits in with the over-all objectives of the conference and meets with the approval of the program committee.

Those who wish to make contributions are requested to submit an abstract of 200 to 500 words not later than July 10, giving the name of the intended speaker and the amount of time required for the presentation.

The contents of the papers, to be presented at this conference, should be directed particularly to descriptions and discussions of novel methods of analysis and of instrumental devices that have been utilized in determining the concentration of trace constituents in those materials involved in the construction and operation of nuclear reactors, and in the analysis of products of nuclear radiation and reactions.

1. *Spectrochemical and X-Ray Methods of Analysis*
Papers are solicited for presentation at this session on the utilization of the techniques of arc, spark and plasma jet; flame emission; atomic absorption; and chemical separations in the spectrochemical analysis of trace constituents and interstitials. Contributions involving the discussion of the techniques of fluorescence, absorption, electron-probe, diffraction, and small-angle scattering in the X-ray analysis of similar materials are also solicited.

2. *Mass Spectrometric Methods of Analysis*
The papers for this session should cover the utilization of mass spectrometry for determining very low concentrations of oxygen, carbon, etc., in reactor-related materials by the use of isotopic dilution techniques. The isotopic analysis of sub-microgram solid samples, and applications of the spark-source mass spectrograph to sub-part-per-million constituents are also suitable subjects for discussion in this particular session.

3. *Nuclear Methods of Analysis*

Papers describing techniques of nuclear analysis and radiochemistry applied to the determination of trace constituents are specifically solicited. Methods of activation or of isotopic dilution analysis would be particularly appropriate. As in the past, papers are solicited that deal with problems of interest and timeliness in nuclear technology. Burn-up determination, radioactive measurement techniques, and improvements in radiochemical separations are topics on which such presentations could be made.

4. *Gas Chromatographic Methods of Analysis*

Selected papers, generally pertinent to analytical problems in nuclear technology, should include new gas chromatographic techniques, applications and potential applications for the determination of trace constituents. Topics to be considered will include the analysis of interstitial gases evolved by conventional analytical operations, the measurement of trace impurities in gases with emphasis on improved detectors, techniques for the separation or concentration of isotopes and potential techniques for the determination of traces of metallic impurities as volatile chelates or halides.

5. *Determination of Carbon, Hydrogen, Oxygen and Nitrogen in Metals*

This session will be devoted to the presentation of papers on methods of hot extraction, vacuum fusion, inert gas fusion, neutron or charged particle activation, combustion methods of separation followed by conductometric, volumetric or manometric methods of measurement, and on any other novel methods of chemical analysis that may be submitted for consideration. Discussions on the comparison of different methods are also invited. The emphasis in these papers should be placed on techniques for the measurement of constituents in concentrations below the 100-p.p.m. level.

6. *Determination of Trace Constituents by Diverse Methods*

Papers are solicited for presentation at this session on methods of analysis, not specifically covered in the other sessions, for determining a broad variety of trace constituents. Discussions on the utilization of such techniques as spectrophotometry and the manifold aspects of electro-analysis, and on applications of other devices or instrumental techniques are broadly indicative of the subject matter which is intended for presentation under this title.

Exhibition of modern analytical instruments and laboratory equipment

Facilities will be available to manufacturers and dealers in laboratory equipment for the installation of 14 exhibits on modern developments in analytical instrumentation and equipment. Information concerning the availability of and rental charges for exhibit space may be secured by writing directly to R. L. Wesley, Oak Ridge National Laboratory, P. O. Box X, Oak Ridge, Tenn. 37831, U.S.A.

General information

The registration fee, except for full-time students, is $5.00 per person.

Proceedings of the conference will *not* be published; however, abstracts of all papers will be published and made available to all persons attending the conference.

Abstracts of papers and any inquiries concerning the conference, including requests for the program and copies of the printed abstracts, should be directed to the Oak Ridge National Laboratory, P. O. Box X, Oak Ridge, Tenn. 37831, U.S.A. Attention: C. D. Susano, Chairman.

Reservations for lodging should be made by direct communication with: The Mountain View Hotel, Gatlinburg, Tennessee 37738, U.S.A.

The conferences will be held in the Huff House of the Mountain View Hotel. Registration will begin in October 5 at 4:00 p.m. in the hotel lobby and continue each day for the duration of the conference. The sessions will begin at 9:00 a.m. daily.

THE FARADAY SOCIETY

An informal discussion on *The Electrical Double Layer in Surface and Colloid Chemistry* is to be held in The School of Chemistry, University of Bristol, on 21st and 22nd September 1964.

Further details can be obtained from Dr. R. H. Ottewill, Department of Physical Chemistry, University of Bristol, Bristol 8, England.

REPORT FOR DISCUSSION AND COMMENT

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RAYMOND DEFAY, NORBERT IBL, EUGÈNE LEVART, GIULIO MILAZZO, GABRIEL VALENSI and PIERRE van RYSSELBERGHE

I. GENERAL DEFINITIONS

(4) The electric tension between a point 1 and a point 2 is equal to the electric potential at the point 1 less that at the point 2.

(5) The electric potential difference between points 1 and 2 is the electric potential at point 2 less that at point 1.

The electric potential difference is thus equal in magnitude but opposite in sign to the electric tension.

II. ONE-PHASE ELECTROCHEMICAL SYSTEMS

(1) The *outer electric potential*, ψ, of a conducting phase having a uniform boundary surface is that defined by the ratio w/q where w is the work done when a point charge q without associated matter is brought infinitely slowly from infinity to a point in vacuum close to the surface of the conducting phase immediately beyond the practical range of the image forces*. This quantity is measurable.

(2) In order to transfer the charge q considered in II(1) from the point where the outer potential has been defined to a point in the bulk of the phase, the existence of a layer of charges and of oriented dipoles means that an amount of work w' must be done against macroscopic coulombic forces. The limit of the ratio w'/q when q tends to zero is the *surface electric tension*, χ.

This tension is positive when, in crossing the surface layer, the electric potential increases from the outside to the inside of the phase.

(3) The *inner electric potential*, ϕ, at a point in a phase is equal to the sum of the outer electric potential and the surface electric tension

$$\phi = \psi + \chi$$

This quantity is definable in principle but generally not measurable.

III. TWO-PHASE ELECTROCHEMICAL SYSTEMS

(1) An *electrode* is an electrochemical system composed of at least two phases in contact, of which one is an electronic conductor and one an ionic conductor. This

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* The image force is the electrostatic force acting between a charge outside a conductor and this conductor as a result of the electrostatic charge induced in the conductor by the said external charge.

system must be the site of an *electrode reaction,* that is, a reaction between constituents of the different phases and in which occurs a transfer of charge from one of the phases to another. We consider in this section only electrodes having a single electrode reaction.

The phases of the electrode are represented by a diagram and numbered from left to right, *e.g.,*

$$\text{Zn} \mid \text{Zn}^{2+} \quad \text{or} \quad \text{Zn}^{2+} \mid \text{Zn}$$
$$\text{1} \quad \text{2} \quad\quad \text{1} \quad \text{2}$$
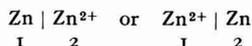
The electrode reaction may be written in either of two ways for either of these diagrams

$$\text{Zn}^{2+}(1) \rightarrow \text{Zn}^{2+}(2) \quad \text{or} \quad \text{Zn}^{2+}(2) \rightarrow \text{Zn}^{2+}(1)$$
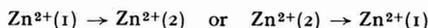
(2) In a more restricted sense the term 'electrode' is often used for the metallic phase in a metal–electrolyte or metal–solution system.

(5) The *Volta tension* of phase 1 with respect to phase 2 is equal to the outer electric potential of phase 1 less that of phase 2 when these two phases are in contact.

(6) The *Galvani tension* of phase 1 with respect to phase 2 is equal to the inner electric potential of phase 1 less that of phase 2 when these two phases are in contact.

(8) When, starting from a given initial state, a reaction proceeds so that the number of moles of each product formed is equal to the stoichiometric coefficient in the reaction written, it is said that the reaction has proceeded by a *unit of advancement.*

(9) The *reaction charge* of an electrode reaction is the charge in faradays carried from phase 1 to phase 2 by this electrode reaction when the latter proceeds by a unit of advancement, *i.e.,* it proceeds once from left to right. The reaction charge may be positive or negative.

(10) The *electrochemical free enthalpy* of an electrode reaction is equal to the algebraic sum of the electrochemical potentials* of the participants multiplied by their respective stoichiometric coefficients which are positive for products and negative for reactants.

(11) The *electrochemical affinity,* $\tilde{A}$, of an electrode reaction is the quantity defined in the preceding definition with the opposite sign:

$$\varDelta \tilde{G} = \sum_i \sum_\alpha \nu_i{}^\alpha \tilde{\mu}_i{}^\alpha = -\tilde{A}$$

At electrochemical equilibrium, $\tilde{A}$ and $\varDelta\tilde{G}$ are zero.

(12) The chemical free enthalpy and the chemical affinity of an electrode reaction are expressed as a function of the chemical potentials of the participants in the same way as the electrochemical free enthalpy is of the electrochemical potentials.

$$\varDelta G = \sum_i \sum_\alpha \nu_i{}^\alpha \mu_i{}^\alpha = -A$$

(14) The chemical enthalpy, H, of an electrode reaction is equal to the algebraic sum of the partial molar chemical enthalpies of the participants each multiplied by their respective stoichiometric coefficients

$$\varDelta H = \sum_i \sum_\alpha \nu_i{}^\alpha h_i{}^\alpha .$$

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* For the definition of the electrochemical potential, see the full report, definition II5b. $\tilde{\mu}_i{}^\alpha = \mu_i{}^\alpha + z_i F\phi^\alpha$ where $\tilde{\mu}_i{}^\alpha$ is the electrochemical potential of species i in phase α, $\mu_i{}^\alpha$ is its chemical potential, z_i its charge, F the faraday and ϕ^α the inner electric potential of phase α.

(18) In all the preceding definitions the order of the phases may be chosen arbitrarily as well as the sense in which the reaction is written. The signs of the quantities defined above will be related to these choices.

In the following definitions of electrode tensions the order of the phases is fixed conventionally according to the diagram: metal(I)/solution(II), the sense in which the reaction is written remaining arbitrary.

(19) The *electric tension of an electrode** is equal to the inner electric potential of the metal(I) less that of the solution(II). It is thus a Galvani tension [see III(6)]

(20) If, for a given chemical and electrical state of an electrode, the electrode reaction is written in the reverse direction without changing the order of numbering the phases, the quotient $\tilde{A}/zF$ is invariant in magnitude and in sign.

Like the electrochemical affinity itself, this quotient is non-zero only away from equilibrium. In the case of a simple electrode it will be called the electrochemical tension of the electrode.

(21) If, for a given chemical state of an electrode, the electrode reaction is written in the reverse direction without changing the order of numbering the phases, the quotient A/zF is invariant in magnitude and in sign.

In the case of a simple electrode this quotient will be called the chemical tension of the electrode.

(22) The reversible, or equilibrium, electric tension of a simple electrode is equal to minus the chemical tension of this electrode, *i.e.*, to $-A/zF$.

At equilibrium the sum of the chemical tension and the electric tension is zero.

Away from equilibrium the electric tension differs in magnitude from the chemical tension. The sum of the chemical tension and the electric tension is then equal to the electrochemical tension defined in III(20) and is now not zero.

The various tensions defined above express the tendency, whether the origin be electrochemical, chemical or electrical, for positive charges to pass from the metal (phase I) to the solution (phase II). Equilibrium, *i.e.*, the absence of net charge transfer between the phases, occurs when the electric and chemical tendencies compensate. The electrochemical tension is then zero, the chemical and electric tensions are equal in magnitude but opposite in sign.

We represent the electrochemical tension between phases I and II by $\tilde{\varepsilon}^{I/II}$, the chemical tension by $\varepsilon^{I/II}$ and the electric tension (or Galvani tension) by $g^{I/II}$. We have in general

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

with

$$\varepsilon^{I/II} = A/zF \quad \text{and} \quad g^{I/II} = \phi^I - \phi^{II}$$

At electrochemical equilibrium

$$g_{rev.}^{I/II} = -\varepsilon^{I/II} = -A/zF, \ \tilde{\varepsilon}_{rev.}^{I/II} = 0$$

In general

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

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* The 'electric tension of the electrode' and the following 'electric tension of a galvanic cell' are the quantities usually called 'electrode potential' and 'cell potential'. We consider the name 'electric tension' clearly preferable.

IV. GALVANIC CELLS

(1) Galvanic cells consist of conducting phases in contact, two at a time, of which at least one is an electrolyte or a solution of electrolyte and having terminal phases which are metallic conductors with identical physical and chemical properties, but in general different inner electric potentials.

(4) The *electric tension of a galvanic cell* is the electric tension of one terminal with respect to the other. It is thus equal to the inner electric potential of the first terminal less that of the second.

Diagrams of galvanic cells consist of the different phases in a defined order. The tension is taken from the first phase to the last.

If we number the phases in the following way:

$1 \mid 2 \mid 3 \ldots \mid 1'$, phases 1 and $1'$ being the terminal made of the same metal, the electric tension U is equal to the difference $\phi^1 - \phi^{1'}$ between the inner potentials of phase 1 and $1'$

$$U = \phi^1 - \phi^{1'}$$

(5) The *cell reaction* is the electrochemical reaction related to the passage of electric current through the cell, *i.e.*, this reaction is the sum of chemical reactions and the electrode reactions associated with this passage. A cell reaction is thus a chemical reaction related to a transfer of charge through the cell. *Consider, for example, the Daniel cell.*

$$Zn \mid Zn^{2+} \mid\mid Cu^{2+} \mid Cu \mid Zn$$
$$\;\; 1 \qquad 2 \qquad\quad 3 \qquad 4 \quad 1'$$
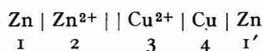
The cell reaction corresponding to passage of current through the phases in numerical order is the following:

$$Zn(1) + Cu^{2+}(3) + 2\, e(1') \rightarrow Zn^{2+}(2) + Cu(4) + 2\, e(1)$$

or

$$Zn^{2+}(1) + Cu^{2+}(3) + 2\, e(1') \rightarrow Zn^{2+}(2) + Cu^{2+}(4) + 2\, e(1)$$

2 e(4)   (handwritten, correcting the crossed-out 2 e(1))
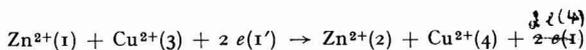
When the electric current changes direction, the cell reaction proceeds from right to left.

The cell reaction in the first from above may be considered as the sum of the three following reactions:

$$Zn(1) \rightarrow Zn^{2+}(2) + 2\, e(1) \qquad \text{at the interphase } 1/2$$

$$Cu^{2+}(3) + 2\, e(4) \rightarrow Cu(4) \qquad \text{at the interphase } 3/4$$

$$2\, e(1') \rightarrow 2\, e(4) \qquad \text{at the interphase } 4/1'$$
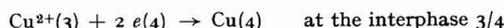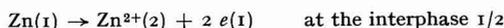
In its second form the cell reaction may be considered as the sum of the three following reactions:

$$Zn^{2+}(1) \rightarrow Zn^{2+}(2) \qquad \text{at the interphase } 1/2$$

$$Cu^{2+}(3) \rightarrow Cu^{2+}(4) \qquad \text{at the interphase } 3/4$$

$$2\, e(1') \rightarrow 2\, e(4) \qquad \text{at the interphase } 4/1'$$
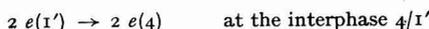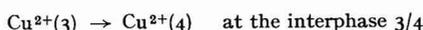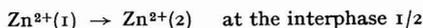
Transfer of ions across the liquid junction is not considered in either form.

When the cell operates in closed circuit, these reactions, in the various forms

above, are accompanied by the transfer of electrons from terminal 1 to terminal 1′ through the external circuit.

(6) The *reaction charge* of the cell, as well as the number of charges transferred in the cell reaction, are defined as in III(9), phases 1 and 2 becoming now the terminals 1 and 1′ of the cell.

(7) The *electrochemical free enthalpy* of a cell reaction is equal to the sum of the electrochemical free enthalpies of the reactions which are summed in the cell reaction.

The electrochemical affinity of a cell reaction, equal to the preceding quantity with the opposite sign is also equal to the sum of the electrochemical affinities of the reactions which are summed in the cell reaction.

In the case of the example given in IV(5):

$$- \Delta \tilde{G} = \tilde{A} = - \sum_i \sum_\alpha \nu_i{}^\alpha \tilde{\mu}_i{}^\alpha = \mu_{Zn}^{\overset{1}{}} + \tilde{\mu}_{Cu^{2+}}^{\overset{3}{}} + 2\, \tilde{\mu}_e{}^{1'} - \tilde{\mu}_{Zn^{2+}}^{\overset{2}{}} - \mu_{Cu}^{\overset{4}{}} - 2\tilde{\mu}_e^{} \; 2\, \tilde{\mu}_e{}^{\prime}$$

or

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

When the interphases 1/2, 3/4, 4/1′ are each in electrochemical equilibrium, the cell as a whole is in equilibrium and $\Delta \tilde{G}$ and $\tilde{A}$ are zero and the reversible electric tension of the cell is given by

$$U_{rev.} = (\phi^1 - \phi^{1'})_{rev.} = (\mu_{Zn^{2+}}^{\overset{2}{}} + \mu_{Cu}^{\overset{4}{}} - \mu_{Zn}^{\overset{1}{}} - \mu_{Cu^{2+}}^{\overset{3}{}})/2\,F + \phi^2 - \phi^3$$

The electric tension $\phi^2 - \phi^3$ is the diffusion tension of liquid 2 and liquid 3. It can sometimes be estimated and separated from the quantity $U_{rev.}$ of the above formula.

(8) The *chemical free enthalpy* of the cell reaction is equal to the sum of the chemical free enthalpies of the reactions which are summed in the cell reaction.

The chemical free enthalpy of the cell reaction is thus equal to the electrochemical free enthalpy of the reaction after removing all terms of the form of a stoichiometric coefficient × molar charge × inner electric potential.

The chemical affinity of the cell reaction is equal to the preceding quantity with the opposite sign.

In the case of the example given in IV(5):

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

At electrochemical equilibrium and neglecting the contribution of the liquid junction potential ($\phi^2 - \phi^3$), the reversible electric tension may be written

$$U_{rev.} = - A/zF$$

since in general

$$\tilde{A} = A + zFU$$

and at equilibrium

$$\tilde{A} = 0 = A + zFU_{rev.}$$

The reversible electric tension of a galvanic cell is thus equal to minus the chemical affinity of the cell reaction divided by the reaction charge. We note that this relation holds whichever direction the cell reaction is written; inversion of the direction corresponds to a change in sign of both the chemical affinity and the reaction charge.

The zero value of the electrochemical affinity in the case of electrochemical equilibrium results from the compensation of the chemical affinity by the electric affinity

(or product of the reaction charge and the electric tension of the cell).

Away from equilibrium, that is, with current flowing, the electrochemical affinity is equal to the sum of the chemical affinity and the product of the reaction charge and the electric tension of the cell.

In cells where the chemically homogeneous phases have ohmic potential differences within them, the electric affinity calculated from

$$\tilde{A} = A + zFU$$

is no longer equal to the sum of the electrochemical affinities of the reaction taking place at the interphases. It is now equal to this sum increased by the product of the reaction charge and the sum of the ohmic tensions between the first and second surface of each phase.

(9) As in the case of an electrode reaction, we call the quotient, $\tilde{A}/zF$, the electrochemical tension of the cell.

The sign of the electrochemical tension is not modified if the cell reaction is written in the reverse order. On the other hand this sign is changed if the order of the phases is reversed.

(10) The quotient A/zF is the chemical tension of the cell.

The sign of the electrochemical tension is not modified if the cell reaction is written in the reverse order. On the other hand this sign is changed if the order of the phases is reversed. This chemical tension of the cell is identical with the quantity usually called the *electromotive force* of the cell in the physicochemical, thermodynamic and electrochemical literature. It represents the action of the chemical (non-electrical) forces while the electric tension represents the action of the electrical forces in the interior of the system. We consider the name 'chemical tension of the cell' to be clearly preferable.

In the case of the diagram of the Daniell cell in IV(5), the chemical tension is positive (except when the ratio of concentrations Cu^{2+}/Zn^{2+} is extremely small). In the case of the opposite diagram (Cu on the left, Zn on the right) the chemical tension would be negative. Thus a positive chemical tension (or electromotive force) represents the action of the chemical forces tending to cause positive charge to travel in the direction of the numbering of the phases $1/2/3/ \ldots 1'$.

(11) It follows from IV(8) that the electric tension of the cell is equal to the electrochemical tension less the chemical tension.

At electrochemical equilibrium the electric tension is equal to minus the chemical tension.

In the case of the Daniell cell written according to IV(5) the electric tension is negative (unless the concentration ratio Cu^{2+}/Zn^{2+} is very small). In the case of the cell written with Cu on the left and Zn on the right, the electric tension would be positive. It may be considered that a positive electric tension implies the existence of chemical forces tending to make positive charge travel in the reverse order in which the phases are numbered $1' \ldots /3/2/1$. The actual movement of the charges is due to the combined action of electrical and chemical forces, *i.e.*, the action of the electrochemical tension.

(12) We return to the case of the Daniell cell. It may be represented by one or other of the two following diagrams:

    (i) $Zn/Zn^{2+}//Cu^{2+}/Cu/Zn$ or (j) $Cu/Cu^{2+}//Zn^{2+}/Zn/Cu$
            1 2   3   4 1'   1 2   3   4 1'

The cell reaction may briefly be written in one or other of the two following forms:

(a) $Cu^{2+} + Zn \rightarrow Cu + Zn^{2+}$ or   (b) $Cu + Zn^{2+} \rightarrow Cu^{2+} + Zn$
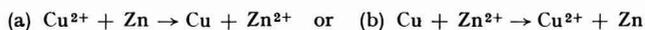
The numbers of charges transferred are

$$z_{1a} = +2, \quad z_{ja} = -2, \quad z_{1b} = -2, \quad z_{jb} = +2$$

The chemical affinities and the chemical free enthalpies of reactions (a) and (b) are related by the following relations:

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

The chemical tension (or electromotive force) corresponding to diagram (i) is given by the four ratios:

$$\varepsilon_i = (+A_a)/(+2\ F) = (-\Delta G_a)/(+2\ F) = (+A_b)/(-2\ F) = (-\Delta G_b)/(-2\ F);$$

while the reversible electric tension corresponding to diagram (i) is given by the four ratios:

$$U_{i,rev.} = (-A_a)/(+2\ F) = (+\Delta G_a)/(+2\ F) = (-A_b)/(-2\ F) = (+\Delta G_b)/(-2\ F)$$

The chemical tension (or electromotive force) corresponding to diagram (j) is given by the four ratios:

$$\varepsilon_j = (+A_a)/(-2\ F) = (-\Delta G_a)/(-2\ F) = (+A_b)/(+2\ F) = (-\Delta G_b)/(+2\ F);$$

while the reversible electric tension corresponding to diagram (j) is given by the four ratios:

$$U_{j,rev.} = (-A_a)/(-2\ F) = (+\Delta G_a)/(-2\ F) = (-A_b)/(+2\ F) = (+\Delta G_b)/(+2\ F)$$

It is easy to verify that

$$U_{i,rev.} + \varepsilon_i = 0 \quad \text{and} \quad U_{j,rev.} + \varepsilon_j = 0$$

Away from equilibrium, but at the given temperature, pressure and chemical composition, the chemical tension (or electromotive force) retains the same value as at equilibrium while the electric tension departs from its reversible or equilibrium value in a direction depending on the direction in which current passes through the cell. If this corresponds to the spontaneous direction of the cell reaction (which is determined by the sign of the purely chemical affinity), the absolute value of the electric tension is smaller than the absolute value of the reversible electric tension. If the current flow corresponds to the non-spontaneous direction of the cell reaction, the absolute value of the electric tension is larger than that of the reversible electric tension.

(14) The relative electric tension of an electrode is (making allowance for liquid-junction tensions, if they exist) the electric tension of a galvanic cell consisting successively of: the metal and the solution of the electrode being studied; the solution and metal of a reference electrode; and finally a terminal of the same metal as that of the electrode being studied.

Such a galvanic cell is called a tensiometric cell.

(18) The standard electric tension of a simple electrode at a given temperature and pressure is the value which its relative electric tension would have in a state of electrochemical equilibrium in which the chemical potential of each constituent in

the electrode reactions were numerically equal to the standard chemical potential of that constituent at the given temperature and pressure.

If the reference electrode of the tensiometric cell is itself in such a state, the standard electric tension $U°$ and the standard chemical tension $\varepsilon°$ corresponding to the electrode being studied are given by

$$U° = - \varepsilon° = \Sigma_i \Sigma_\alpha v_i \mu_i°/zF = - A°/zF = \Delta G°/(zF),$$

the summation being taken over all reactants and products of the reaction of the tensiometric cell; $A°$ is the standard chemical affinity and $\Delta G°$ the standard chemical free enthalpy of this cell reaction.

The numerical values of the standard electric tensions depend on the choice made, for the dissolved substances, between molalities, molarities or mole fractions and equally on the choice of reference electrode. We note in this connection that the divergence of electric tension between analogous electrodes in which the solutions are of molality m, and molarity m is of the order of a tenth of a millivolt in the case of dilute aqueous solutions.

Standard electric tensions may be used to place the different electrodes in a tension series.

(19) The reference electrode usually chosen is the standard hydrogen electrode at one atmosphere, *i.e.*, a reversible hydrogen electrode in which the hydrogen ions are at unit activity and the gaseous hydrogen has a pressure of one atmosphere.

(21) The reversible or equilibrium values of relatives electric tensions with the sign defined in VI(11) ('European') when multiplied by F are equal to the chemical affinities of reduction reactions written in the direction such that $\frac{1}{2} H_2$ at $p_{H_2} = 1$ atm, becomes H^+ at $a_{H^+} = 1$

$$\tfrac{1}{2} Zn^{2+} + \tfrac{1}{2} H_2 \rightarrow \tfrac{1}{2} Zn + H^+ \tag{i}$$

In the cell (i)

$$U_{i,rev.} = A_{red.}/F = U_{rev.,eur.}$$

Similarly the reversible or equilibrium values of relative electric tensions with the so-called American signs multiplied by the faraday are equal to the chemical affinities of oxidation reactions

$$\tfrac{1}{2} Zn + H^+ \rightarrow \tfrac{1}{2} Zn^{2+} + \tfrac{1}{2} H_2 \tag{j}$$

In cell (j)

$$U_{j,rev.} = A_{oxid.}/F = U_{rev.,amer.}$$

VI*. ELECTROCHEMICAL KINETICS AND POLARIZATION

(1) At the contact of the two phases of an electrode [see III(1)] there exists an *interfacial region* having properties (chemical, electric, hydrodynamic) different from those existing in the depth of the two phases.

We consider here only those electrodes of which phase I is metallic.

The interfacial region comprises, going from I to II, a *transfer layer* followed by a *diffuse layer* which is itself followed during the passage of a current by a *diffusion layer*. At electrochemical equilibrium the diffuse layer is followed by a uniform section of phase II.

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* Section V in the original is entirely omitted in this abbreviated version.

(2) The *transfer layer* is an adsorption layer in which the electrons take part in the electrode reaction. The properties of this layer may have discontinuities.

(3) The *diffuse layer* is the part of the electrolyte or of the solution in which, whether or not a current is flowing, there exists in every point a non-zero charge density and a non-zero gradient of electric potential and of chemical potential.

The fall of electric potential in the diffuse layer is the *electrokinetic tension*, ζ, called usually, *electrokinetic potential*.

(4) The *diffusion layer* is the part of the electrolyte or of the solution in which, when a current flows, the composition is different from that in the depth of phase II, the gradients of electric and chemical potentials being considerably weaker than in the diffuse layer and the electric charge density being everywhere practically negligible or zero.

The diffusion layer extends to infinity in the absence of all convection. Its thickness depends essentially on the agitation and on the natural convection forces (such as gravity).

For all non-negligible currents the thickness of the diffusion layer is considerably greater than that of the diffuse layer.

(5) The *electrochemical double layer* is formed, even in the presence of current, of the transfer layer and of the diffuse layer (the diffusion layer being excluded); it is thus the only part of the interfacial region where the local electric charges are not zero and the charge density varies with distance from the electrode.

(6) The *electric tension of an electrode passing current* must be considered as the electric potential of metal I less that of the solution at the limit of the diffusion layer.

The *relative electric tension* of this electrode is experimentally accessible [see IV(14)], but is subject to some uncertainty resulting from the ohmic potential drop between the end of the Haber-Luggin capillary and that of the diffusion layer.

(8) When a given electrode reaction transfers a positive charge to the metal of the electrode, the corresponding current is defined as *cathodic*, and the reaction itself is called *cathodic* or a *reduction*. When this reaction transfers a negative charge to the metal, the corresponding current is defined as anodic and the reaction itself is called *anodic* or an *oxidation*.

(9,11) The current corresponding to an electrode reaction, or the *reaction current*, is the algebraic sum of an anodic component and a cathodic component crossing the transfer layer simultaneously in opposite directions.

(10) At electrochemical equilibrium the anodic and cathodic components of the reaction current in the transfer layer are equal in absolute value. This common value is called the *exchange current*.

(12) The *reaction current density* of an electrode reaction is taken as the current divided by the *apparent area* of the electrode surface.

(13,14,15) The *density of the electrochemical reaction velocity* is equal to the reaction current density divided by the reaction charge. It can be separated into the *densities of the velocities of the anodic and cathodic transfer reactions*. Dividing the latter by the concentrations of the reacting species taken in the positions and raised to the powers suggested by the analysis of the reaction mechanism, one obtains the corresponding *reaction rate constants*.

These, at the given temperature and pressure, depend on the local electric tension and contain the activity coefficients of the reactants and of the activated complex;

they are not necessarily independent of the composition.

(16) One calls qualitatively *polarization* the whole of the effects of the passage of the current which cause the electric tension of an electrode (or that of a galvanic cell) to be different from its value under a total current of zero.

Quantitatively the *polarization of a cell* is defined as the electric tension during the passage of a current less its value under a total current of zero.

The *experimental polarization* of an electrode is equal to its *relative electric tension* with current flow [see (6)] less its value in the absence of a current. It is called *anodic* when its value is positive and *cathodic* when its value is negative.

(17) When, at a given current density, an electrode is the site of a definite and unique reaction, its *overtension* at a given instant is equal to its relative electric tension at that instant, less the reversible electric tension corresponding to this reaction. This reversible or equilibrium electric tension is that which the electrode possesses at electrochemical equilibrium and for the same chemical state of the phases as that corresponding to the instant at which the overtension is measured.

In the case of the simple electrode considered here the experimental polarization differs from the overtension only by the ohmic term mentioned in (6).

(18,19) If several electrode reactions having distinct reversible electric tensions occur simultaneously at the same electrode, the electric tension of this electrode is called a *mixed electric tension*. One can evaluate an *overtension* with respect to the reversible electric tension of each of these different reactions.

(21) The overtension η of a metal–solution electrode I/II is identical to its electrochemical tension and is related to the electrochemical affinity of the electrode reaction by the formula $\eta = \tilde{A}/zF$, zF being the reaction charge.

Consider for example, the reaction $X^{x+}(\mathrm{II}) + x\,e(\mathrm{I}) \to X(\mathrm{I})$.

Its electrochemical affinity can be separated into three parts corresponding to the passage of X^{x+} across the diffusion layer, to the passage of X^{x+} across the diffuse layer and to the neutralization of X^{x+} by x electrons to form X in the transfer layer. The total overtension can then be separated into three terms: the *overtension of electrochemical diffusion*, the *overtension in the diffuse layer* (probably negligible in the presence of a supporting electrolyte of sufficient concentration), the *transfer overtension*, which in the case considered here may also be called the *activation overtension*.

(22) When the overtension of electrochemical diffusion is negligible, the overtension of an electrode reaction, above a threshold value of the order of some millivolts, is often a linear function of the logarithm of the absolute value of the current density. Such a relation is called *Tafel's Law*. Thus one writes for the anodic and cathodic cases respectively

$$\eta_a = a_a + b_a \ln i \quad \text{and} \quad |\eta_c| = a_c + b_c \ln |i|$$

One assumes generally that these relations apply to the anodic component i_a and the cathodic component i_c of the resultant current density $i = i_a - |i_c|$ even in the neighbourhood of equilibrium. One has then, at the electrical tension, $(U_{\mathrm{rev.}} + \eta)$, common to both components,

$$i = i_0 \left[\exp(\beta_a F\eta/RT) - \exp(-\beta_c F\eta/RT) \right]$$

where

$$i_0 = \exp(-a_a/b_a) = \exp(-a_c/b_c)$$

defines the absolute value of the *exchange current* [see (10)] and

$$\beta_a = RT/Fb_a \quad \text{and} \quad \beta_c = RT/Fb_c$$

multiply, in the expression for i, the electrochemical affinity divided by the number of charges transferred $(\tilde{A}/z = zF\eta/z = F\eta)$.

(23) If the reaction in the transfer layer occurs in a series of elementary steps the *stoichiometric* number of each of these steps is the number of times it occurs when the total reaction occurs once. When one of these steps is the sole rate-determining step it is useful to put the coefficients β_a and β_c in the forms

$$\beta_a = (|z|/\gamma)\alpha_a \quad \text{and} \quad \beta_c = (|z|/\gamma)\alpha_c$$

in which γ is the stoichiometric number of this rate-determining step. The coefficients α_a and α_c are then called the *transfer coefficients*.

(24) If, in the curve which represents the current density as a function of the applied electric tension, this density reaches a value which cannot be exceeded without changing the electrode reaction, this value is called the *limiting current* density of this reaction. It corresponds to the maximum velocity of transport of matter related to this reaction in the given experimental conditions (hydrodynamic regime, concentration in the bulk of the solution). In the case when a dissolved species is consumed in the electrode reaction (the case of metal deposition for example, in the presence of a supporting electrolyte) the limiting current is reached when the concentration of this species becomes negligible at a point where the diffusion layer meets the diffuse layer.

(25) A *simple electrode* is called *reversible* when an overtension, however small, is accompanied by a *non-zero* stationary current. If, on the other hand, a small overtension does not cause any stationary current, the electrode is called *indifferent*.

(26) For a poly-electrode the reversibility must be considered relatively to each of the possible reactions at this electrode.

The poly-electrode can be *reversible* relatively to one reaction and *indifferent* relatively to another.

(27) The electric tension of a simple electrode for which the current density of anodic polarization is equal to the sensitivity of its own measurement, can be called the oxidation electric tension for the specified sensitivity. The reduction electric tension can be similarly defined.

In the limiting case of a reversible simple electrode these tensions coincide and their common value is then the oxidation–reduction electric tension or the redox electric tension.

SUMMARY

This is an abbreviated version of the report already published in this Journal (2 (1961) 265–290 and 6 (1963) 173) and was prepared by G. MILAZZO and P. VAN RYSSELBERGHE. The translation into English was prepared by R. PARSONS and is presented here in order that a wider group of electrochemists and electro-analytical chemists may become aware of the direction in which Nomenclature discussions are taking. Comments direct to C.I.T.C.E. (Professor Pierre van Rysselberghe, Department of Chemistry, Stanford University, Stanford, California, U.S.A.) or (if in publishable form), to this Journal, will be welcome.

ELECTROCATALYSIS

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I. INTRODUCTION

Fundamental studies in electrocatalysis have hitherto been few[1]. Except for those on the hydrogen evolution reaction (h.e.r.)[2-7], most studies of the mechanism of electrochemical reactions have been limited to one or a very few metals. It may be regarded as premature to attempt already a synthesis of the limited knowledge in the field as it is at present.

The following indicate the possibilities in electrochemical energy conversion, the realization of which depend principally upon improvement of the position in electrocatalysis.

(1) Only three years ago, few chemists anticipated the electrochemical oxidation to CO_2 of a substance as inert as ethane, at temperatures $< 100°$ [8]. The complete electrochemical oxidation of cellulose to CO_2 at the same low temperature is perhaps even more surprising[9]. One is reminded of the ease with which a number of complex biochemical reactions occur at body temperatures with the aid of enzymatic catalysts[10].

(2) Electrochemical rate constants for the same reaction on different metals are very wide-spread, *e.g.*, about 10^{10} for the hydrogen evolution reaction[11] and about 10^5 for the oxygen evolution[12] and metal dissolution reactions[13]. The value to which it is worthwhile attempting to increase the exchange current density, (i_0), is the limiting current density due to mass transport. The order of magnitude of this in amps cm^{-2}, at room temperature in well-agitated aqueous solutions is (for reactions at planar surfaces) roughly equal to the solubility of the reactant in moles l^{-1}.

Thus, the value of the exchange current density for the oxidation of C_2H_4 to CO_2 on platinized platinum in 1 N H_2SO_4 at $80°$ is 10^{-8} [14]. The solubility of C_2H_4 at $80°$ in this solution is $\sim 2 \cdot 10^{-3}$ moles l^{-1}. Hence, the overpotential for this reaction will remain negligible (energy conversion efficiency $\approx 100\%$) up to a rate at which the oxidation becomes controlled by mass transport if the exchange current density were increased to about 10^{-3} A cm^{-2}, *i.e.*, if the heat of activation were reduced by about 14 kcals $mole^{-1}$.

(3) The practical usefulness of electrochemical generators is a function not only of energy conversion efficiency but also of the power per unit area or weight. The effect of catalysis on this position is shown in Table 1. The calculations of *maximum feasible* performances are ideal in the sense that they neglect probable increases in weight

TABLE 1

THE POSSIBLE EFFECT OF CATALYSIS ON THE POWER PER UNIT AREA AND WEIGHT OF CERTAIN ELECTROCHEMICAL CONVERSION SYSTEMS

System	$T°$	Watts cm⁻² present best	HP lb⁻¹ present best	Watts cm⁻² adequate catalysis	HP lb⁻¹ adequate catalysis	Watts cm⁻² maximum feasible	HP lb⁻¹ maximum feasible	HP lb⁻¹ ordinary i.c. engine (air)
				(1)		(2)		
H_2–O_2	67	0.154[15]	0.023	0.250	0.038	0.250	0.539	
C_2H_6–O_2	150	0.010[8]	0.005	0.025	0.012	0.025	0.042	
Decane–O_2	110	0.011[16]	0.005	0.040	0.019	0.040	0.067	1.0
$Hg(K)$–K	300	0.179[17]	0.004	0.575	0.011	0.575	0.532	
Li–LiCl–KCl–Cl_2	450	—	—	—	—	1.05	1.878	

(1) Calculated from weight of cell, including present electrodes and solution as in (1), but with zero activation overpotential, working in solutions without marked agitation.

(2) Calculated by assuming that weight of system is twice the weight of electrodes, 0.002-cm thick and density 3 which together with solution between them are assumed to be 0.1-cm thick, and with marked solution agitation.

necessary to allow for heat transfer at relatively high power densities. The power per unit weight which would be attainable with adequate electrocatalysis would be that of dynamic conversion.

II. FACTORS INFLUENCING ELECTROCHEMICAL CATALYSIS

1. Pre-requisites for rational development of catalysts

Reasoning cannot effectively be applied to a system unless the rate-determining step at least, and preferably also the path of the reaction, have been elucidated.

The principal characteristic of electrocatalysis is its potential dependence. The rate does not increase with potential in the same way for all mechanisms for a given overall reaction. Hence, catalyst A will be faster than B, for a given reaction, at an overpotential, η_1, but the situation will be reversed at overpotential, η_2 (Fig. 1). Thus, one
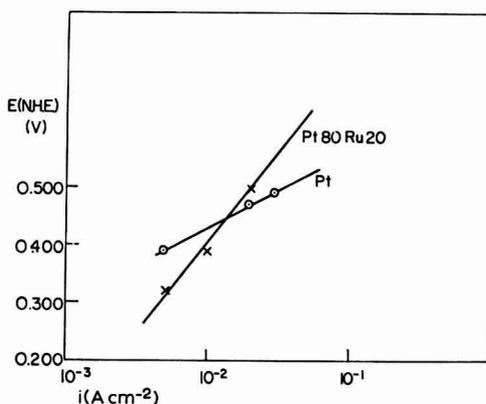
Fig. 1. Current–potential relation for ethylene on Pt and $Pt_{80}Ru_{20}$ alloy in $1\ M$ H_2SO_4, $120°$, $P_E = 1$ atm.

must decide upon some potential at which the current density per true unit area is a rational measure (for comparison purposes) of the catalytic power of the given electrode. The most reasonable potential is that of zero charge[18-20], for here, no charge-dependent field affects the reaction rate.

Reaction rate at the potential of zero charge on a series of electrocatalysts represents a fundamental way of comparing catalytic power; it compares the thermal part of the electrochemical catalysis, i.e., k_0 in the equation:

$$k = k_0 \exp[\pm (V - V_{p.z.c.})F/RT] \tag{1}$$

where $V_{p.z.c.}$ is the potential of zero charge. Hence, a knowledge and an interpretation of k_0, although important to the understanding of catalytic power, is insufficient to predict the polarization at a given potential.

It is important to note the necessity of avoiding competing reactions, when discussing the potential dependence of k. This is particularly so in oxidation reactions. An example is in Fig. 2[1], where the competing oxide formation on Ir and Rh shuts off ethylene oxidation at current densities too low for reasonable performance of these substrates as anodes in hydrocarbon fuel cells. The same shut-off occurs on Pt at higher potentials, thus permitting the current densities to increase to a more useful

value. For a given desired oxidation reaction, the thermodynamic reversible potential must be at least, say, 0.5 V more negative than the reversible potential of the next anodic reaction possible in the system concerned.

An important pre-requisite is knowledge of adsorption of the reactant and its
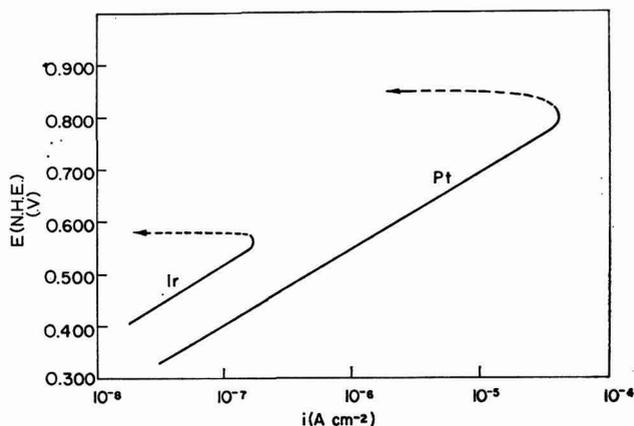
Fig. 2. Limits of the potential region of ethylene oxidation on Pt and Ir.
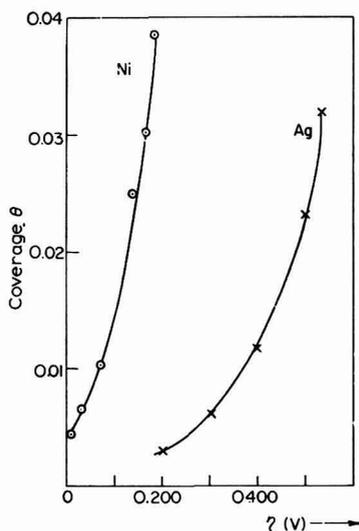
Fig. 3. Dependence of the hydrogen coverage on potential for Ni and Ag.

dependence on potential. This is available for a few cases for H[21,22] (Fig. 3), and for O[1] (Fig. 4). The adsorption of organic substances on Hg has only recently been reported[23]. The potential-dependence of butyl compounds is shown in Fig. 5. Plots of the adsorption of butyl-, phenyl- and naphthyl-compounds (under comparable potential conditions) with a number of substituents[23] are shown in Fig. 6; the variation of adsorption with structure is up to 10^4 times.

Only a few papers concerning adsorption of organic substances on solid metals have appeared[24,25], or are about to be published[26,27]. In Figs. 7 and 8, adsorption of naphthalene and decylamine on Ni[26,27] is shown as a function of potential. Sub-
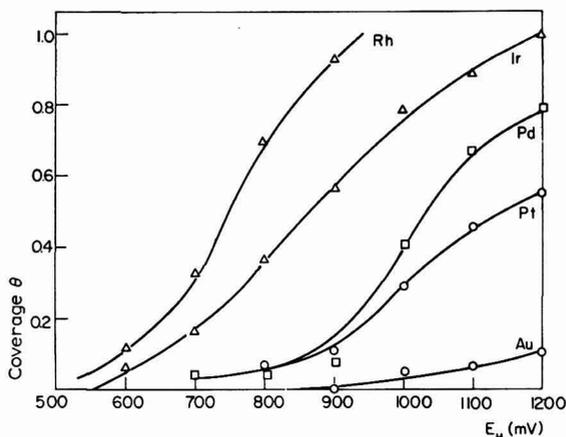
Fig. 4. Coverage with O as a function of potential on various noble metals.
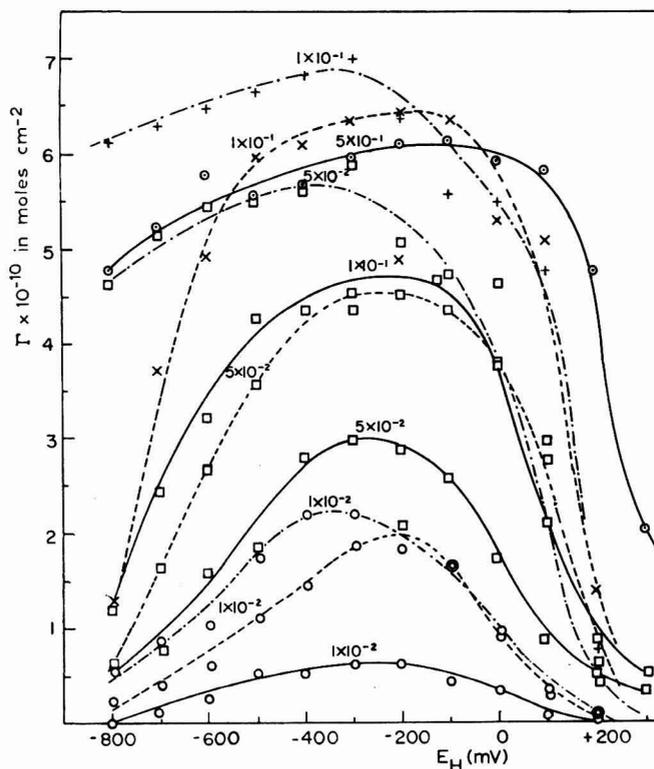
Fig. 5. Γ_A as a function of E_H for constant adsorbate concentrations and $C_{HCl} = 0.1\ N$: (a, ——) n-butyl alcohol; (b, – – –) n-valeric acid; (c, –·–·–) n-valeronitrile. (C_A stated on figure).

stances react on electrodes only if the potential for the region in which adsorption is appreciable (region as small as 0.4 V[24], Fig. 9) coincides with a potential region (for oxidation) positive to the reversible redox potential for the indicated reaction. There has been little discussion of this obvious point because of lack of data.

2. Factors which may increase rate constant

An understanding of such factors is at present limited to the following:

(a) *Electronic factors.* The comparative rates expected for a given reaction on sub-
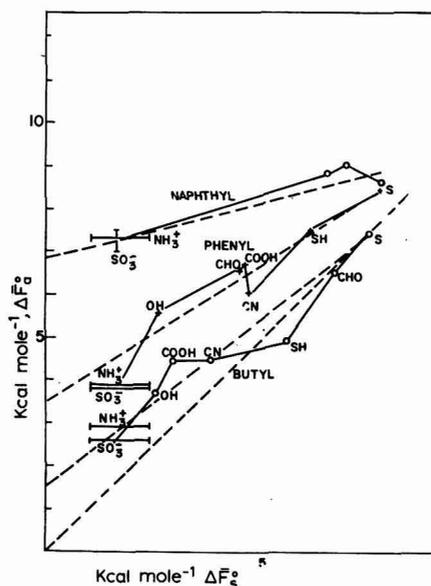
Fig. 6*. $\Delta \bar{F}_a^\circ$ at the p.z.c. and $\theta = 0.25$, as a function of $\Delta \bar{F}_s^\circ$.

Potential of nickel electrode in mV (N.H.E.)
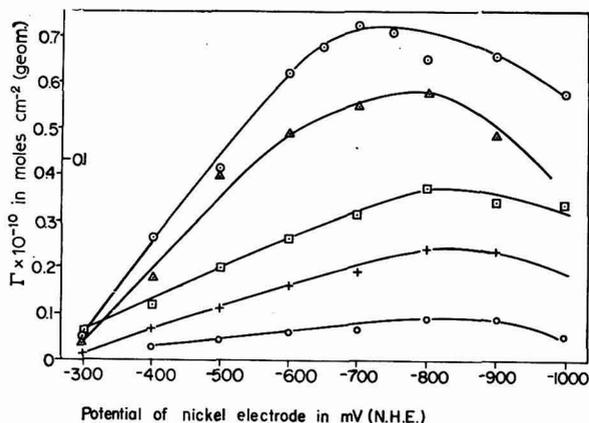
Fig. 7. Adsorption of naphthalene on nickel from 1 N NaClO$_4$, pH = 12, at the following concns. of naphthalene: $\odot$, 7.5 × 10^{-5}; $\triangle$, 5.6 × 10^{-5}; $\square$, 3.8 × 10^{-5}; +, 1.9 × 10^{-5}; $\circ$, 0.8 × 10^{-5} M.

* $\Delta \bar{F}_a^\circ$ is the net free energy of adsorption; $\Delta \bar{F}_s^\circ$ is the molar free energy of dissolution (cf. ref. 23).
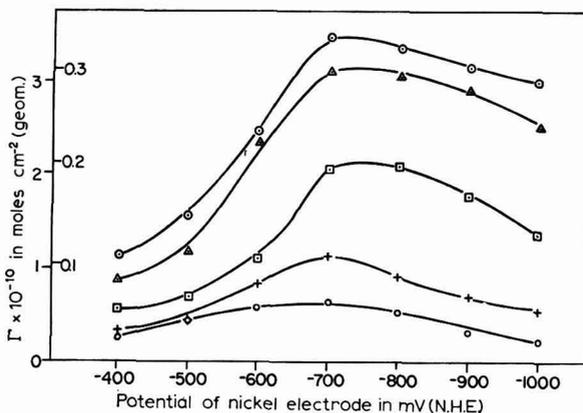
Fig. 8. Adsorption of n-decylamine on nickel from 1 N NaClO$_4$, pH $= 12$, at the following concns. of n-decylamine: $\odot$, 7.5×10^{-5}; $\triangle$, 5.0×10^{-5}; $\boxdot$, 2.5×10^{-5}; $+$, 1.0×10^{-5}; $\bigcirc$, $0.5 \times 10^{-5} M$.
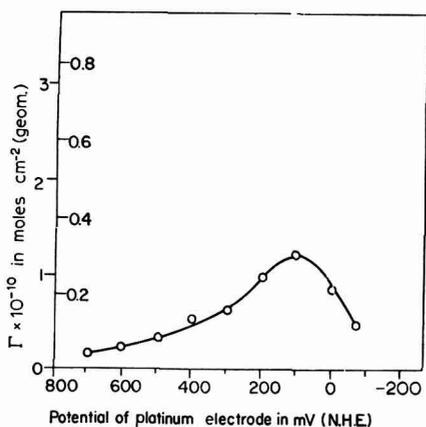
Fig. 9. Adsorption of naphthalene on platinum from 0.9 N NaClO$_4$; 0.1 N HClO$_4$; 2.5×10^{-6} M naphthalene.
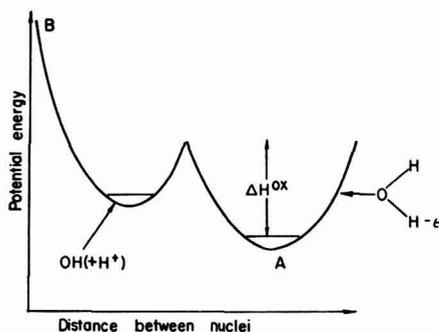
Fig. 10. Potential energy–distance relation for water discharge.

strates of different d-character and work function can be evaluated theoretically, so long as the rate-determining step in the considered reaction is known. Suppose that the reaction concerned is the oxidation of ethylene to CO$_2$ and that the rate-determining reaction is the discharge of H$_2$O to form adsorbed OH radicals[14], which then undergo a series of further reactions with adsorbed organic molecules. Then, the standard free energy of activation for the charge-transfer reaction of a water molecule to the electrode is the principal quantity which determines the rate. The major contribution to this is the heat of activation for the charge transfer. If this be classical*, a potential energy profile diagram can be used to indicate the comparative effect of the work function, Φ, and adsorption energy (Fig. 10).

These remarks refer to the potential of zero charge, and in changing the substrate

* It has been so assumed in the electrochemical literature up to the present time, after the early suggestions to the contrary by GURNEY[28] (cf. BUTLER[29], but also cf. HUSH[30]).

to attempt to follow a tendency, deduced from considerations of the potential-energy barrier for some elucidated rate-determining step, the counter effect of change of potential from the (changed) potential of zero charge must be taken into account.

(b) *Surface configuration.* If the necessary mechanism determination has shown that (e.g., for an organic oxidation reaction) the breaking of a bond is rate-determining, the geometric factors will have effects parallel to those in chemical catalysis.

There is evidence to show that an increase in the defect concentration is important in increasing catalysis in some electrode reactions, e.g., the oxidation of H_2[15]. Mechanism studies on anodic hydrogen dissolution are insufficient to allow mechanistic interpretation of this fact. However, it is suggestive that if 0.1% C is introduced into zone-refined Fe, the rate constant for the charge transfer to protons is increased about ten times[31]. The local work function is less at a defect than on crystal planes. Were the charge transfer rate-determining and to occur predominantly at points occupied by defects associated with carbon, the experimental result could be understood. One of the difficulties of study of the effect of trace inclusions in a substrate is that normally only the bulk concentration is known and Gibbs adsorption will cause the added component to be increased or decreased in the surface with respect to that in the bulk.

(c) *Alloys.* Alloys change *d*-character. Introduction of a second component may

TABLE 2[32]

COMPARISON OF THE CATALYTIC ACTIVITY OF Pt-BLACK AND NOBLE METAL ALLOYS IN METHANOL OXIDATION

Metal or alloy	Polarization in 2 N H_2SO_4 at 100° at 20 mA cm^{-2} (V)	Remarks
Pt-black	0.44	
Binary alloys of Pt with- (i) base metals-		
of Group IVB and VB	0.37–0.39	Best: Pt67 Mo33 - 0.20
VIB and VIIB	0.20–0.38	Pt80 Re20 - 0.29
		Pt67 Re33 - 0.31
Fe, Ni, Co, Be, Pb, Cu, Bi, Sb	Similar, or decreased activity as compared with Pt-black	
(ii) *noble metals*		
Ru	0.24–0.32	Optima for 20% Ru-(Pt Ru) 33% Ru-(Ru₂Pt)
Os	0.30–0.35	
Rh	As Pt-black	
Ir (25%)	0.33	
Binary Pt-free alloys		
Ru — Rh	0.29–0.38	Optimum for Ru 90 Rh 10
Ru with Pd, Ir, Rh	0.38–0.46	
Os, with Pd, Ir, Rh		
Ternary alloys of Pt + Ru with-		
W	0.25–0.37	
Ta	0.24–0.27	
Zr	0.30	
Mo	0.23	(Pt 70 Ru 15 Mo 15)

increase the number of surface defects; if the less noble component (*e.g.*, Mo in Pt) is an atom undergoing easy redox-potential changes in solution, it may set up a redox system in the double layer, which allows a change of path of the overall reaction to one having a lower heat of activation. None of these mechanisms has been systematically investigated. Systematic information on alloy effects is scarce except for methanol oxidation[32]. Several binary and ternary alloys containing Pt, or of other noble metals, exhibit higher catalytic activity than does platinized-Pt (Table 2). There is some evidence to show that to some extent the catalytic activity in methanol oxidation is paralleled in oxidation of other fuels, since Pt–Ru based catalysts exhibit improved activity for oxygenated and paraffinic hydrocarbons. The enhanced catalysis alloys in methanol oxidation cannot be explained by physical properties such as surface area, since this is, for example, about the same for the active Pt–Ru alloys (Table 2) as for Pt-black. However it is difficult to relate the catalysis to merely electronic factors, since a number of metals in ternary alloys with widely varying electronic characteristics perform equally well in binary compositions. Activation energies for oxidation on Pt and Pt–Ru alloys are also similar.

It is thus probable that increase in the concentrations of surface defects on the alloyed catalyst, compared with the pure metal, gives the origin of the catalysis.

(*d*) *Semi-conductor surfaces.* Electrode kinetics on semi-conductors has been formulated fairly recently[33-37], and the use of boride-[38] and carbide-[39] electrodes in oxidation reactions was first reported in 1963. Ni_2B proved to be a good catalyst in hydrazine oxidation[40] (0.1 V less polarization than Pd). As an anode in H_2 oxidation at 80°, it showed only 40 mV higher polarization than a Pd/graphite anode in the range from 65–260 mA cm^{-2} [38].

The catalytic activity of Ni_2B seems to be connected primarily with its chemisorptive properties. Coverage with hydrogen varies from zero to unity (0–1) at one extreme to no change in coverage from zero coverage (0–0) at the other extreme, depending on the thermal pre-treatment of the electrode, whilst the reaction rate decreases about 10^6 times.
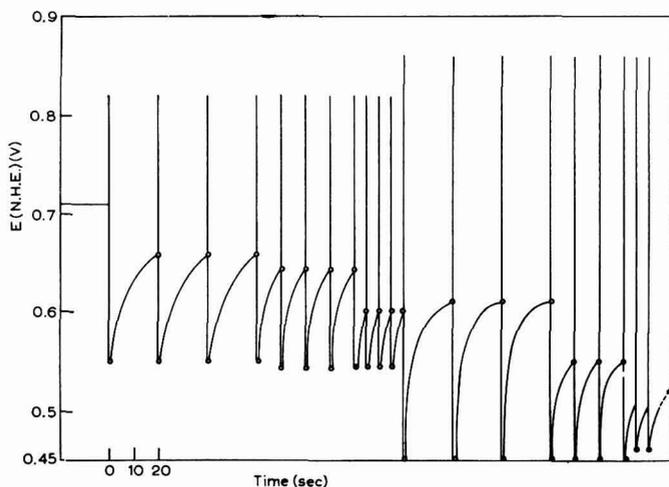
Fig. 11. Effect of anodic pulses on the steady-state potential for ethylene oxidation on platinum with $i = 1$ mA/cm^2, showing variation of pulse amplitude and repetition time.

Control of the electron energy levels in a semi-conductor by the choice of suitable donor- and acceptor-species makes possible a particular well-controlled model system for work in electrocatalysis.

(e) *Imposed pulses of potential*. Suitable pulses (say, an anodic pulse to cover the electrode with O and a cathodic pulse to remove this layer, with a pulse time of 10^{-3} sec) should clean the surface from inhibiting impurity layers which may build up there, and hence maintain catalysts of constant activity. There is the possibility that grain growth can also be controlled because the size of grains which nucleate is potential-dependent. Whether the imposing of repeated pulses can bring about increase in catalysis, apart from removal of impurities, is not established. In principle, the momentary dissolution of surface atoms, *i.e.*, the creation of defects, should be attainable.

The effect of pulsing on the anodic overpotential for ethylene oxidation[53] is shown in Fig. 11. Pulsing may be effected by short circuiting the cell for about 0.1 sec in every 20 sec.

3. *Use of redox systems to change the path of the overall reaction*

Considering, for example, the oxidation of methanol to CO_2, and that the rate-determining step in this reaction is charge transfer from CH_3OH to the substrate, catalytic effects should be observed if a redox couple is present which has (a) a standard potential in the neighborhood of the reversible potential; (b) i_0 values for charge transfer much greater than those exhibited by the direct charge transfer from the organic; (c) a sufficiently high rate constant for the subsequent homogeneous phase oxidation. Then:

$$M^{2+} \rightarrow M^{3+} + e \text{ (at electrode)}$$

$$2 \, M^{3+} + CH_3OH \rightarrow HCHO + 2 \, M^{2+} + 2 \, H^+ \text{ (in solution)}$$
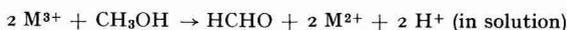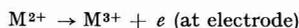
etc.

This principle can be successfully applied (with the nitrous–nitric couple, having an e_0 of 0.94[41]) in overcoming the difficulties[42] associated with making practical reversible oxygen electrodes, where the i_0 involved in the oxygen dissolution reaction is of the order of 10^{-10} amps cm^{-2}. A similar principle might be used to reduce the overpotential which needs to be applied to hydrogen–oxygen generators, *e.g.*, the manganous–manganic couple, which has a standard redox potential in acid solution of 1.5 V[41].

4. *Photo-, sono-, radioactive and radio-galvanic effects*

The basic theory of photo-[42] and sono-effects[43,44] has been known for some time. Large photo-effects (decreases of overvoltage by 0.5 V) have been observed upon u.v. irradiation of Si[45]. Significant acceleration of the oxygen reduction reaction by α-emitters dissolved in the substrate has been established, but the interpretation is not clear[46,47].

III. THE MECHANISM OF HYDROCARBON OXIDATION

The oxidation of hydrocarbons at low temperatures has recently attracted a great deal of interest. However, the literature[48–50] is concerned predominantly with technological aspects.

TABLE 3

DIAGNOSTIC CRITERIA FOR OXIDATION OF HYDROCARBONS ON Pt AT 80° IN 1 N H_2SO_4

Hydrocarbon	Tafel slope	% Coulombic efficiency for complete oxidation	Exchange current density ($A\ cm^{-2}$)	$\left(\dfrac{di}{dp}\right)_{V,pH}$	$\left(\dfrac{d\log i}{d\log c_{H+}}\right)_V$	$\left(\dfrac{dV}{d\log c_{H+}}\right)_i$ (mV)	$\left(\dfrac{d\eta}{d\log c_{H+}}\right)_i$ (mV)	$\left(\dfrac{d\log i_0}{d\log c_{H+}}\right)$
Ethylene	$\dfrac{4.6\,RT}{F}$	100	$4\ \times 10^{-8}$	<0	-0.45	65	0–10	~ 0
Allene	$\dfrac{4.6\,RT}{F}$	93	2.9×10^{-8}	<0	-0.41	68	0–10	~ 0
Propylene	$\dfrac{4.6\,RT}{F}$	97	2.5×10^{-8}	<0	-0.35	52	0–20	~ 0
1-Butene	$\dfrac{4.6\,RT}{F}$	71	1.8×10^{-8}	<0	-0.47	67	0–10	~ 0
2-Butene	$\dfrac{4.6\,RT}{F}$	83	1.8×10^{-8}	<0	-0.45	66	0–10	~ 0
Acetylene	$\dfrac{2.3\,RT}{F}$	100	10^{-18}	<0	-0.8	~ 50	0–20	~ 0

Investigation of the reaction mechanism was started at the University of Pennsylvania about three years ago[14,51,52,54]. The mechanism of oxidation of several olefins (ethylene[14], propylene, allene, 1-butene, 2-butene[54]) and of acetylene[51] has been studied on platinum at 80°.

Apart from small differences in i_0 and coulombic efficiency, the electrochemical behavior and main reaction products were similar for all olefins (Table 3) and the mechanism of their oxidation will be discussed taking ethylene as example.

1. Oxidation of ethylene (as representative of olefins)

The overall reaction yields CO_2 with $100 \pm 1\%$ coulombic efficiency in acid and $90 \pm 5\%$ efficiency in alkaline solution. Thus, branching reactions leading to products other than CO_2 and water (or protons) are neglected* and the half-cell reaction can be written as:

$$C_2H_4 + 4 H_2O \rightarrow 2 CO_2 + 12 H^+ + 12 e \tag{3}$$
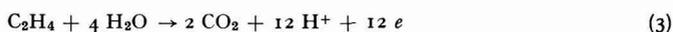
The observed Tafel slopes for the pH range 0.3–12.5 and pressure range from 10^{-3} to 1 atm are $b = 140$–160 mV (Figs. 12, 13). At 80°, the theoretical value of b $(=2.3 \times RT/\alpha F)$ for $\alpha = 0.5$, is 140. Thus, a charge transfer is the rate-determining step (r.d.s.) and the value of α is in the range 0.44–0.5.
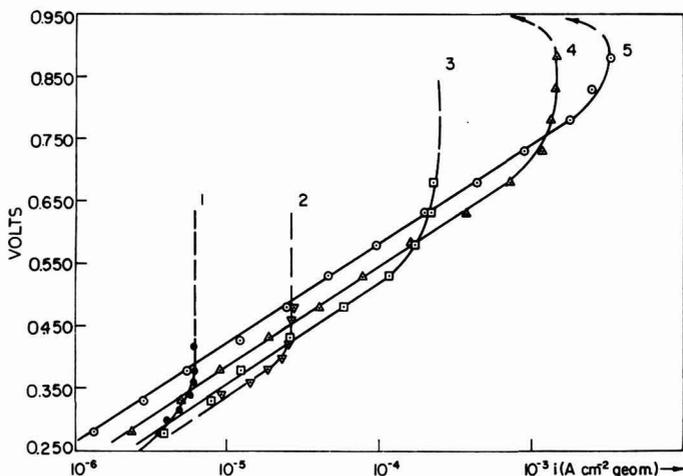
Fig. 12. Current–potential relation for ethylene oxidation on Pt (pH = 0.5) as a function of ethylene partial pressure: (1), $P_E = 10^{-4}$ atm; (2), 10^{-3} atm; (3), 10^{-2} atm; (4), 10^{-1} atm; (5), 1 atm.

The observed Tafel slope is consistent only with the first charge transfer, or a later charge transfer from the species present at the electrode at full coverage, as the step which determines the rate of the overall reaction. In the latter case, no pressure effect could be expected.

This however exists (Fig. 12) in the sense that the steady-state reaction velocity

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* However, a branching reaction of a current efficiency below that which can be detected in acid solutions could occur and inhibit catalysis increasingly with increasing time (see below).

decreases with increase of pressure. Thus the value of $b = 2.3 \times 2\, RT/F$, together with the fact that $di/dp < 0$, fix the location of r.d.s. as the first charge-transfer reaction.

The inverse pressure effect could be caused by a build-up of a side-product, possibly a polymer, of the reaction. The evidence on this hypothesis is not yet conclusive, but
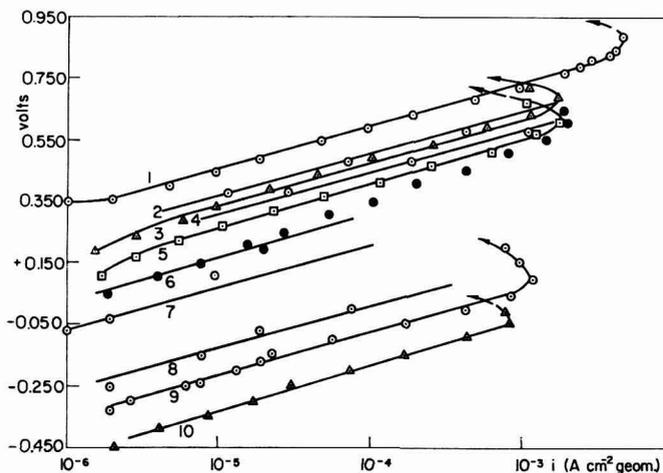
Fig. 13. Current–potential relation for ethylene oxidation on Pt ($P_E = 1$ atm) as a function of pH: (1), 0.5; (2), 1.9; (3), 2.3; (4), 2.9; (5), 3.45; (6), 5.6; (7), 6.5; (8), 9.8; (9), 10.8; (10) ,12.5.

its balance appears to be negative. Thus, the pressure effects are reversible on repeated pressure changes without hysteresis. Similar effects have been observed on Pt with other hydrocarbons, but not during ethylene oxidation on some other noble metals where positive pressure effects occur, with a radically different dependence of current density upon potential, *i.e.*, a different mechanism*.

The negative pressure effect, $di/dp < 0$, shows that the r.d.s. involves a substance which will only absorb if the surface is *free* of ethylene (or any intermediate derived therefrom). Thus the likely rate-determining step is one of the two reactions:

$$H_2O \rightarrow OH + H^+ + e \tag{4}$$

$$OH^- \rightarrow OH + e \tag{5}$$

The reaction sequence may then be represented by

$$C_2H_4 \rightleftharpoons C_2H_4\ ads \tag{6}$$

or r.d.s.
$$H_2O \rightarrow OH_{ads} + H^+ + e \tag{4}$$

$$OH^- \rightarrow OH_{ads} + e \tag{5}$$

$$C_2H_{4\,ads} + OH_{ads} \rightarrow C_2H_4\,OH \ (or\ C_2H_3 \cdot + HOH) \tag{7}$$

$$C_2H_4OH + \ldots \rightarrow \ldots 2\,CO_2 + 11\,H^+ + 11\,e \tag{8}$$

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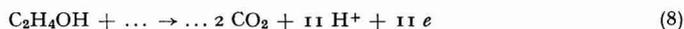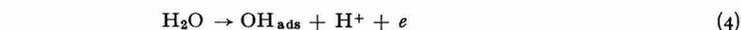
* However, it is noteworthy that the mechanism discussed here does depend in an important way upon the conclusions that the pressure effects arise directly as a result of the mechanism and not as a consequence of secondary inhibition. It is desirable to obtain further evidence on this point.

This deduction can be shown to be consistent with the negative pressure effect in the following way. According to the hypothesis, the coverage of all intermediates will be negligible in comparison with the coverage by the ethylenic radical, since they occur *after* the rate-determining step and are not in equilibrium because of the constant removal of the final product, CO_2. Thus it is justified to assume that $\theta_{total} \sim \theta_{ethylene}$.

The model for ethylene adsorption under anodic conditions deduced on the basis of considerations of the energy of adsorption, is

$$C_2H_4(sol) \rightarrow \begin{array}{cc} CH_2\!-\!CH_2 \\ | \quad\quad | \\ Me \quad Me \end{array} \qquad (9)$$

Thus, the adsorption of ethylene molecules involves four surface sites of Pt per one molecule of ethylene. The adsorption isotherm is then of the form

$$\frac{\theta}{(1-\theta)^4} = K_p P_E \qquad (10)$$

where $\theta = \Gamma/\Gamma_{max}$ is the fractional coverage with ethylene; K_p the equilibrium constant (atm^{-1}); P_E the partial pressure of C_2H_4. On the basis of independent radioactive measurements[55], the coverage of Pt with organic θ_E was estimated to be relatively potential invariant in the potential range of Tafel region, and equal to ~ 0.7. For this value of θ at $P_E = 1$ atm, $K_p \approx 86$ atm^{-1}.

Now for the postulated mechanism, the current is given by:

$$i = k_2 a_{H_2O} (1 - \theta_E) \exp[\alpha FV/RT], \quad \text{or} \qquad (11)$$

$$i = k_2 a_{OH^-} (1 - \theta_E) \exp[\alpha FV/RT], \qquad (12)$$

and at constant potential, the current decreases with pressure as does the term $(1 - \theta_E)$.

From the theoretical plots of $(1 - \theta)$ *versus* P_E, for $K_p = 150$ atm^{-1}, the values of $(1 - \theta)$ at $P_E = 1$, 0.1, 0.01 and 0.001 atm were found and introduced into eqn. (11). The term $k_2 a_{H_2O} e^{\alpha FV/RT}$ was calibrated from the experimental value of i at $P_E = 1$ atm and 530 mV and the theoretical i–log p relationship was plotted for seven potential values which are shown in Figs. 14 and 14a. The points correspond to the experimental data, and are in fairly good agreement with the theory.

Further support for the hypothesized mechanism is as follows. Independently of the number of carbon atoms, of the number of double bonds, and their position in the olefins studied, the kinetic parameters remain the same, and the exchange current changes by less than a factor of 2 (Table 3). This is strong support, for, were the rate-determining charge transfer to include an organic radical, i_0 should change significantly with structure.

Whether H_2O or OH^- takes part in the rate-determining charge transfer can be discussed in terms of the log i–pH relationship (Fig. 15). The value of $(d \log i/d \text{ pH})V$ is constant over the whole pH range, suggesting that the same mechanism applies in both acidic and alkaline solutions. Charge transfer from OH^- ions would cause, in acid solutions, a limiting-current at low current densities. Thus discharge occurs from water molecules.

The present model is not consistent with the theoretical coefficients (derived on a
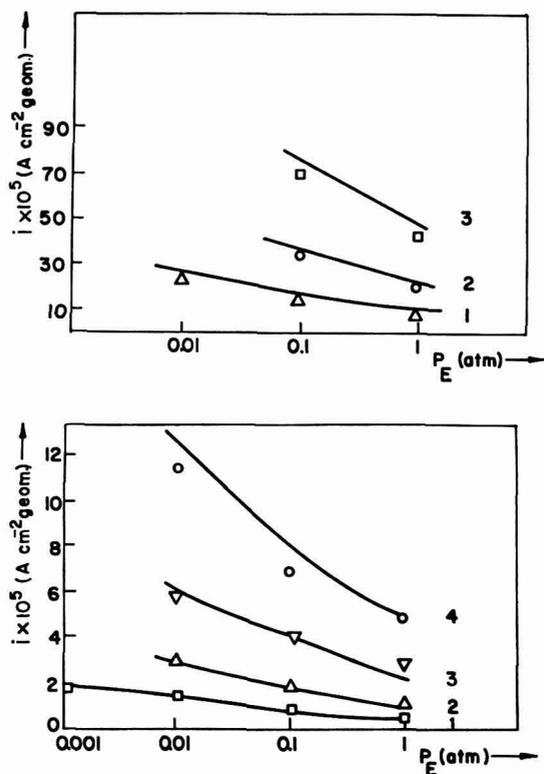
Fig. 14. Current as a function of ethylene partial pressure at constant potential for ethylene oxidation on Pt, pH = 0.5: (1), 0.38 V; (2), 0.43 V; (3), 0.48 V; (4), 0.53 V.

Fig. 14a. As Fig. 14 with: (1), 0.58 V; (2), 0.63 V; (3), 0.68 V.
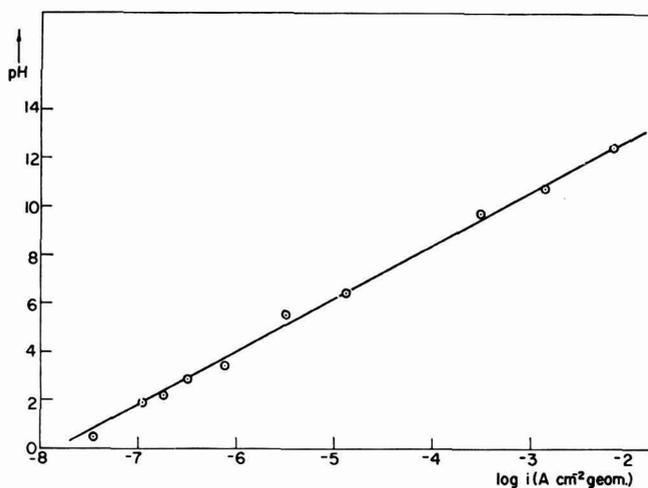
Fig. 15. Current ($V = 0.1$ V) as a function of pH for ethylene oxidation on Pt.

TABLE 4

EXPERIMENTAL AND THEORETICAL pH DEPENDENCE IN CERTAIN REACTIONS INVOLVING
THE DISCHARGE OF H_2O OR OH^- IN PRESENCE OF EXCESS NEUTRAL SALT

Origin		$\left(\dfrac{d \log i}{d\,pH}\right)_V$	$\left(\dfrac{d\eta}{d\,pH}\right)_i$	$\left(\dfrac{d \log i_0}{d\,pH}\right)$
Theoretical consideration	Discharge from water	o	RT/F	$-\alpha$
of the simple model	Discharge from OH^-	I	$-RT/F$	α
BOCKRIS AND HUQ[56],				
O_2 evolution on Pt, (H_2SO_4)		0.25	$\alpha RT/F$	
VETTER AND BERNDT[57],				
O_2 evolution on Pt, wide pH-range			o	
MacDONALD AND CONWAY[12],				
O_2 evolution on Pd and Au alloys $(H_2SO_4, NaOH)$			o	o
WROBLOWA, PIERSMA AND BOCKRIS[14]		0.45	$\sim$ o	$\sim$ o

simple model) for water or OH^- ion discharge as the rate-controlling step (Table 4). This fact does not militate against the suggested mechanism but lends it support because similar anomalous pH effects were observed by authors[12,56,57] (Table 4) who were concerned with simple reactions in which the probability of rate-determining charge transfer from H_2O is very high.

2. Effect of the oxide formation

In the oxidation on Pt of paraffins[58], olefins[14,54], as well as of acetylene[51], under potentiostatic conditions, the current drops to negligible values at $V \approx 0.9-0.95$ V (against the hydrogen electrode in the same solution), and does not increase until the potential of O_2 evolution is reached. On the other noble metals, this *passivation* occurs at different potentials (*cf.* Fig. 16), which always coincide with the potential
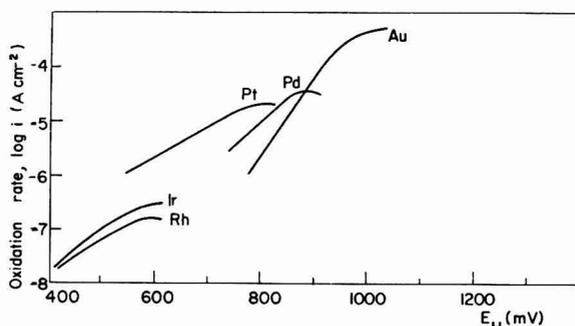
Fig. 16. Current–potential relation for ethylene oxidation on various noble metals (80° in 1 N H_2SO_4).

at which ~ 0.2 of the electrode surface is covered with oxygen. The observed passivation with respect to ethylene oxidation may be understood if at potentials above $V \approx 0.9$ V, the reaction between OH radicals, or OH and H_2O occurs fast enough for the accumulation of PtO (or $Pt(OH)_2$), and water discharge on to the PtO covered surface drops to a negligible rate.

IV. THE MECHANISM OF ELECTROCATALYSIS

1. Hydrogen

A crude interpretation of the trends in acid solutions was suggested by CONWAY AND BOCKRIS in 1957[11]. This was based upon plots of η (c.d. 10^{-3} A cm^{-2}) against the value (for most metals *calculated*), of the metal–hydrogen bond strength (see Fig. 17). One clear group is discernible (the transition-metals) and a second group (Hg, Pb, Tl) exists with a weak indication of the direction of the dependence of η upon D_{MH}. The latter group of metals do, in any case, have i_0 values which are very different, in orders of magnitude, from those which the transition-metals have at comparable D_{MH} values. The few points on these low i_0 metals are at least not incon-
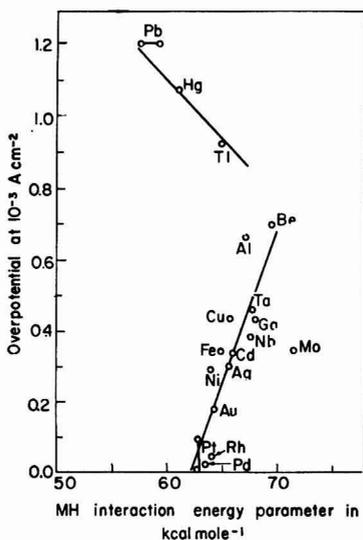
Fig. 17. Plot of overpotential against metal–hydrogen-bond strength for various metals.
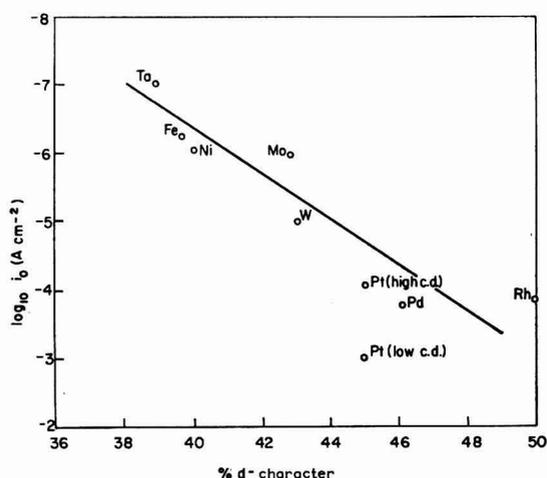
Fig. 18. Log$_{10}$ i_0 for the hydrogen evolution reaction as a function of d-character of the metal.

sistent with the view that, for them, i_0 becomes larger as the MH bond strength increases. Conversely, for the transition-metals, i_0 decreases as D_{MH} increases. Correspondingly (Fig. 18), for the transition-metals a relation between the exchange current density values and the number of d-vacancies exists, in the sense that i_0 decreases as the number of d-vacancies increases.

These correlations would seem to favor the proton-discharge reaction as rate determining on Hg, Pb and Tl, and the desorption reaction with charge transfer, rate-determining for the transition-metals. Thus (see Fig. 19), if the potential energy
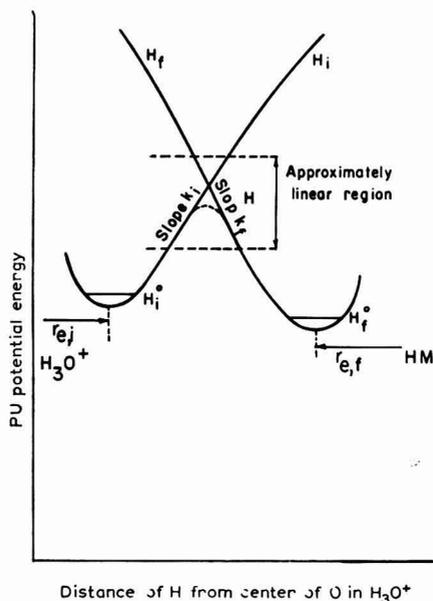
Fig. 19. Potential energy diagram for the discharge process $H_3O^+ + M + e \rightarrow MH + H_2O$.
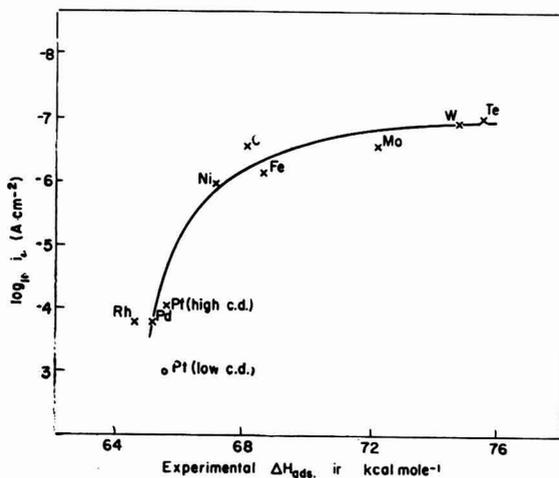
Fig. 20. $\log_{10} i_0$ for the hydrogen evolution reaction at various metals as a function of the experimental values for heat of adsorption of H at these metals.

of the final state for proton discharge is lowered (higher bond strength), the rate at a given potential will increase; but for electrochemical desorption as a rate-determining step, it will be (Fig. 20) more difficult to carry out the reaction as the MH bond strength increases.

The noble metals form a third group in the discussion by CONWAY AND BOCKRIS[11]; under conditions in which their i_0 values are sufficiently high ,the h.e.r. is determined by the atomic combination reaction[59,60]. There is some controversy concerning the mechanism of hydrogen evolution on the noble metals. Thus, BREITER[5], supported by FRUMKIN[61], regards the rate-determining step as the diffusion of molecular H_2 in solution away from the electrode. It is clear that at a sufficiently high i_0 for the charge transfer and desorptive reactions, a diffusion-step must become rate-determining. The question is, how high must the i_0 for the hydrogen evolution reaction on noble metals be, for the overall reaction to be no longer controlled by the chemical combination step. In the region of current density when bubbles form, rate control by diffusion of H_2 away from the surface does not appear to be an acceptable rate-determining mechanism. Bubbles usually form in hydrogen evolution at current densities of about 10^{-3} A cm^{-2}.

Several criticisms may be made of the CONWAY AND BOCKRIS analysis.

(i) The rates are compared at the reversible potentials, whereas they should be compared at the potential of zero charge[18-20], (although some of these are not available).

(ii) The values of the H-bond strength with which the rates of the h.e.r. at the reversible potentials are compared (those from the gas phase at zero coverage) are not necessarily the valid ones. The bond strength decreases with increase of surface coverage in a gas-phase reaction. For the rate-determining reaction $H^+ + e \rightarrow H_{ads}$, the θ values are expected to be relatively low[2,21,62], and hence the values used are probably valid for purposes of comparison. But, for the $H^+ + H_{ads} + e \rightarrow H_2$ reaction, the surface coverage in the steady state is probably high, and the values would be lowered compared with those used in the plot in Fig. 17.

The last criticism may perhaps be met when it is recalled that the coverage is likely to be of the same order (>0.9) on all metals, for the h.e.r. under conditions of rate-determining $H^+ + H_{ads} + e \rightarrow H_2$. The *differences* between the heats of adsorption from H on a series of transition-metals would then *follow* D_{MH}[3].

(iii) Lastly, the values of $(i_0)_H-(i_0)_D$ on Fe (a metal which is with CONWAY AND BOCKRIS' second class, rate-determining $H^+ + H_{ads} + e \rightarrow H_2$) are not consistent with this reaction. However the position of this metal in the log i_0–ΔH graph, compared with the log i_0–D_{MH} line for Hg, Pb and Tl, makes it possible that Fe is a proton-discharge case[3].

The CONWAY AND BOCKRIS view of 1957 makes a consistent picture of the relative efficacy of catalysts for the h.e.r. and one for which the difficulties are not insuperable. It has been developed by others[63]. The next approximation should take into account the effect of interactions between H atoms on the surface and deal with the question of tunnelling.

2. Hydrocarbons

Facts concerning ethylene oxidation on Pt, Ir, Rh, Au and Pd[1] are summarized in Table 5. The relative rates are shown in Fig. 16.

TABLE 5

ETHYLENE OXIDATION AND CHARACTERISTIC PROPERTIES OF THE METALS

	Reaction product	"Chemical" reaction rate at p.z.c.* (A/cm^2)	pH dependence $\left(\dfrac{dE}{dpH}\right)_s$	Tafel slope $\left(\dfrac{dE}{2.3d\log i}\right)_{pH}$ (mV)	Lattice parameter $Q[\mathring{A}]$ (from 64)	Potential of zero charge $\Delta\varphi$ p.z.c. (hydrogen scale)	Vacant d-orbitals per atom (from 65)	Heat of sublimation I_s (kcal mole^{-1}) (from 66)
Platinum	CO_2	$1 \cdot 10^{-7}$	70	160	c.f.c. 3.914	$+0.30$[67,68]	0.55	135
Iridium	CO_2	$1 \cdot 10^{-11}$	75	132	c.f.c. 3.823	$+0.05 \pm 100^+$	1.5	165
Rhodium	CO_2	$5 \cdot 10^{-11}$	70	155	c.f.c. 3.794	$+0.05 \pm 100^+$	1.5	138
Gold	no CO_2 aldehydes	$1 \cdot 10^{-11}$	0	72	c.f.c. 4.070	$+0.30$[69,70]	0	84
Palladium	no CO_2 aldehydes	$7 \cdot 10^{-10}$	0	80–110	c.f.c. 3.879	$+0.25$[68]	0.55	91

* Potential of zero charge (formerly, e.c.m.).

+ Calculated using electronic work functions in the following eqn. (cf. ref. 1): $\varphi_{M_1} - \varphi_{M_2} = \Delta\varphi_{M_1}{}^\circ - \Delta\varphi_{M_2}{}^\circ$, where φ_M = electronic work function, $\Delta\varphi_M{}^\circ$ = potential of zero charge.

Group I (Pt, Ir, Rh) oxidizes ethylene to CO_2 quantitatively, shows a Tafel slope of $2\,RT/F$ and has $(\partial \ln i/\partial \mathrm{pH})_E \approx \alpha$. Group II (Au, Pd) gives incomplete oxidation, and exhibits a Tafel slope nearer to RT/F than to $2\,RT/F$ and has $(\mathrm{d}\ln i/\partial \mathrm{pH})_E = 0$.

For the first group, the M–O bonds have a strength greater by 20 ± 5 kcal mole^{-1} from that of Group II. Incomplete oxidation with Au and Pd can be more easily understood, than with Pt, Ir and Rh, because the intermediate products would have a higher rate of desorption.

Interpretation of the relative rates of Au and Pd is difficult because hitherto no mechanism study on these metals has been made. Rudimentary ideas on the mechanism, namely from the current–potential and the pressure effect (positive) suggests a mechanism of the type:

$$C_2H_4 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} C_2H_{4\,ads} \tag{13}$$

$$C_2H_{4\,ads} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} C_2H_4{}^+{}_{ads} + e \tag{14}$$

$$C_2H_4{}^+{}_{ads} + H_2O \underset{\text{r.d.s.}}{\overset{k_3}{\longrightarrow}} C_2H_4OH + H^+ \tag{15}$$

$$C_2H_4OH_{ads} \underset{\text{fast}}{\overset{k_4}{\longrightarrow}} C_2H_4O + H^+ + e \tag{16}$$
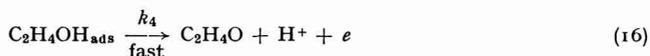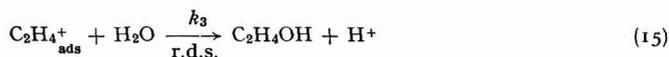
If this type of mechanism is valid for the major contribution to the reaction, the heat of activation will be determined primarily by the heat of adsorption of $C_2H_4{}^+$ and CH_3CHO and also by the thermionic work function. Very roughly, one can suppose that the heat of adsorption of $C_2H_4{}^+$ and CH_3CHO do not greatly differ for a given metal and hence in a first approximation, the influence of the M–C bond strength can be neglected. The work function effect remains. The experimental rates of water discharge at the potentials of zero charge are about 10^2, and the theoretical about 10^3.

On Pt, Ir and Rh, the rate-determining step is probably water discharge, $H_2O \rightarrow OH_{ads} + H^+ + e$. The heat of adsorption and work function would be the main metal-dependent parameters in determining the rate. But the OH and H_2O bonding — and differences thereof on each metal — would tend to cancel. Hence, one might expect again principally a work function dependence. The observed and expected trends are consistent, though the agreement is hardly better than qualitative.

It is a feature of the reactions of the oxidation of hydrocarbons that the coverage with oxide is important and shuts off the reaction (by its formation of an oxide layer) at various characteristic paths (see Figs. 16 and 4).

VI. NEEDED TRENDS IN RESEARCH

1. Adsorption and interactions within adsorbed layers

More information than that given in the initial papers by BOCKRIS AND SWINKELS[26],[27], of the dependence of the adsorption of organic compounds on potential, and upon their own structure and that of the solid metal, is needed.

The O and H adsorption positions on metals have been explored fully only for the noble metals. The importance of knowing the potential dependence of this adsorption is illustrated by the results of DAHMS AND BOCKRIS[1] on the inhibition of the ethylene

oxidation rate when the adsorbed O is replaced by an oxide. The relative rates of the same electrochemical reaction on a metal and a mono-layer of its oxide are not known. A tentative calculation[14] for water discharge on to bright Pt and oxide-covered Pt yielded the ratio of $K_{Pt}/K_{PtO} \approx 10^8$.

Lastly, the equations of state for adsorbed layers on electrodes are unexamined, although a start in this direction has been made by BLOMGREN, BOCKRIS AND JESCH[23]. The importance of such work is exemplified by the findings of CONWAY AND GILEADI[71]; the existence of a sufficiently large interaction between the particles in the final state of a charge-transfer reaction causes a change in the interpretation of the mechanism on the basis of the slope of the Tafel line, and reaction orders.

2. Path and rate-determining step

The work to date is preliminary and needs extension as well as verification by alternative methods. In this respect the interpretation of transient studies is desirable. Tafel slope, pH, and pressure effects, together with a knowledge of $\theta_{organic}$ and θ_0 in the organic oxidation reactions, contribute substantially to mechanism elucidation.

Although the study of half a dozen hydrocarbon oxidation reactions by these methods would be helpful, it would still not allow a solid theory of electrocatalysis of hydrocarbon oxidation (a central topic from the view-point of electrochemical energy conversion) until information on a large number of materials (rationally chosen to evaluate, e.g., the effect of change of lattice parameter; the influence of crystal face orientation; the effect of the d-band characteristics and that of work function) becomes available.

3. Theoretical

Several basic aspects of the theory of electrode kinetics are uncertain.

(a) Theory of β. The model is still obscure.

(b) Work function. Which work function is effective and how is the vacuum-measured value dependent on the water and organic molecule adsorption?

(c) Electronic structure of adsorbed organic compounds. Detailed descriptions of bonding in terms of molecular orbitals offer attractions for predictions concerning the rates of charge-transfer reactions at electrodes.

(d) Structure of the electric double-layer in the presence of adsorbed, reacting entities. How do the water dipoles in the double layer before additions of the organic molecule depend on potential and on the organic adsorption? Where is the reacting entity, outside a layer of adsorbed water or not? To what extent does our fairly good knowledge of the double-layer structure on polarizable interfaces of Hg in aqueous solutions of simple inorganic ions apply to solid electrodes in the presence of organic molecules?

SUMMARY

The factors influencing the rate of electrochemical reactions have been discussed. Choice of the rational potential scale for comparison of the catalytic activity of electrodes is a prerequisite for the systematic development of the electrochemical catalysis. Electronic and surface properties of metals can be altered to enhance electrocatalysis. Examples of other ways of enhancing activity are given.

The mechanism of hydrocarbon oxidation is discussed in the example of ethylene. Discharge of water molecules is the rate determining step for olefin oxidation. Characteristic properties of noble metals for the ethylene oxidation are given. Oxide formation is an important limiting feature in hydrocarbon oxidation.

The mechanism of electrocatalysis is formulated for the hydrogen evolution and hydrocarbon oxidation reactions. For the h.e.r., the exchange current density depends on the d-character of the metal and the heat of adsorption of H. Criticism of this analysis are suggested.

Further study of the fundamentals of organic adsorption and electrode kinetic theory are required. Information of a large number of rationally chosen materials is necessary for a solid theory of catalysis.

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ELECTROCHEMICAL KINETICS OF PARALLEL REACTIONS

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INTRODUCTION

The fundamental quantities which determine the thermodynamic feasibility of a fuel-cell system are the free energy ΔG, and the entropy ΔS of the overall cell reaction and these quantities are related to the reversible potential and its first derivatives with respect to temperature. In some electrode reactions, *e.g.*, the anodic oxidation of ethylene, the overall reaction varies with the catalyst[1] and care has to be taken in respect to the appropriate ΔG and therefore the reversible potential.

Examples of electrochemical reactions in which at least two different products are formed are well known[2-4]. Thus, in such cases the electrochemical reaction may be a branched reaction, or it may be preceded, accompanied or followed by chemical reactions in solution.

Consider a branched reaction

$$A \rightarrow B \overset{\nearrow C}{\searrow D} \tag{I}$$

where the coulombic yields for the formation of C and D are Q_C and Q_D respectively. When the net current is zero, such a system will set up a mixed potential[5] which lies between the reversible potentials E_{A-C} and E_{A-D} for the two overall reactions. A single reversible potential cannot be defined for such a system, particularly when the coulombic yield Q_C and Q_D are potential dependent.

In the treatment below we consider a reaction scheme such as (I), giving rise to two products* and assume that all reactions are activation controlled**.

PARALLEL REACTION SCHEME

Consider an electrochemical reaction of the type (I)

$$A \rightarrow B \tag{II}$$

$$B \rightleftharpoons C \tag{III}$$

$$B \rightleftharpoons D \tag{IV}$$

---

* The extension of this treatment to cases where three or more products are formed is trivial.
**cf. the work of BARD *et al.*[6-8] who considered such effects for diffusion-controlled reactions.

where Step II is rate-determining. The rate equations corresponding to these steps will be

$$v_2 = k_2[\text{A}] \exp\left(\beta_2 z_2 VF/RT\right) \tag{1}$$

$$v_3 = k_3[\text{B}] \exp\left(\beta_3 z_3 VF/RT\right) \tag{2}$$

$$v_{-3} = k_{-3}[\text{C}] \exp\left[-(1 - \beta_3)z_3 VF/RT\right] \tag{3}$$

$$v_4 = k_4[\text{B}] \exp\left(\beta_4 z_4 VF/RT\right) \tag{4}$$

$$v_{-4} = k_{-4}[\text{D}] \exp\left[-(1 - \beta_4)z_4 VF/RT\right] \tag{5}$$

where k_i, β_i and z_i are the specific chemical rate constant, the symmetry factor and the charge transferred in the ith step, respectively*, V is the metal solution potential difference and the solutions have been assumed to be such that the diffuse part of the double layer can be neglected.

At steady state we have

$$\frac{\text{d}[\text{B}]}{\text{d}t} = v_2 - (v_3 - v_{-3}) - (v_4 - v_{-4}) = 0 \tag{6}$$

and hence from eqns. (1–6) the steady state concentration of [B] at the electrode is given by

$$[\text{B}] =$$

$$\frac{k_2[\text{A}] \exp\left(\beta_2 z_2 VF/RT\right) + k_{-3}[\text{C}] \exp\left[-(1 - \beta_3)z_3 VF/RT\right] + k_{-4}[\text{D}] \exp\left[-(1 - \beta_4)z_4 VF/RT\right]}{k_3 \exp(\beta_3 z_3 VF/RT) + k_4 \exp(\beta_4 z_4 VF/RT)}$$

$$\tag{7}$$

The fractional coulombic yields Q_C and Q_D are defined as

$$Q_\text{C} = \frac{i_3 - i_{-3}}{(i_3 - i_{-3}) + (i_4 - i_{-4})} = \frac{n_3(v_3 - v_{-3})}{n_3(v_3 - v_{-3}) + n_4(v_4 - v_{-4})} = \frac{v_3 - v_{-3}}{(v_3 - v_{-3}) + (n_4/n_3)(v_4 - v_{-4})} \tag{8}$$

and similarly

$$Q_\text{D} = \frac{v_4 - v_{-4}}{(n_3/n_4)(v_3 - v_{-3}) + (v_4 - v_{-4})} \tag{9}$$

where i_3 and i_4 are the partial currents for the two parallel steps III and IV; and n_3 and n_4 are the total numbers of electrons transferred in the overall reactions $\text{A} \to \text{C}$ and $\text{A} \to \text{D}$, respectively.

Case 1

We consider first the case when all reverse reactions may be neglected, namely $v_{-3} = v_{-4} = 0$ and derive the various modes of dependence of the rates of the parallel paths on potential and the corresponding coulombic yields.

(a) If Steps III and IV are both *chemical* (*i.e.*, $z_3 = z_4 = 0$ and $n_3 = n_4 = z_1$) we have (from eqns. 2, 4 and 8)

$$Q_\text{C} = \frac{v_3}{v_3 + v_4} = \frac{k_3}{k_3 + k_4} \tag{10}$$

---

* Normally $z = \pm 1$ and it is therefore omitted from the exponential term. In the present treatment $z = \pm 1$ for an electrochemical step and $z = 0$ for a purely chemical step.

and similarly

$$Q_D = \frac{v_4}{v_3 + v_4} = \frac{k_4}{k_3 + k_4} \tag{11}$$

Thus the coulombic yields in this case are independent of potential, but will generally be temperature-dependent.

(b) If Step III is electrochemical but Step IV is purely chemical (i.e., $z_3 = 1$; $z_4 = 0$; $n_3 = z_2 + z_3 = 2$; $n_4 = z_2 + z_4 = 1$) we have

$$Q_C = \frac{v_3}{v_3 + (n_4/n_3)v_4} = \frac{v_3}{v_3 + v_4/2} = \frac{1}{1 + (k_4/2k_3)\exp(-\beta_3 VF/RT)} \tag{12}$$

and

$$Q_D = \frac{v_4}{(n_3/n_4)v_3 + v_4} = \frac{1}{1 + (2k_3/k_4)\exp(\beta_3 VF/RT)} \tag{13}$$

The ratio of coulombic yields is

$$\frac{Q_C}{Q_D} = \frac{1 + (k_4/2k_3)\exp(-\beta_3 VF/RT)}{1 + (2k_3/k_4)\exp(\beta_3 VF/RT)} = (2k_3/k_4)\exp(\beta_3 VF/RT) \tag{14}$$

Since the coulombic yield can be determined in many cases to better than 5%, its variation with potential, according to eqn. (14) could be observed over 300 mV or more*.

(c) If Steps III and IV both depend on potential, but to different extents (i.e., $z_3 \neq 0$; $z_4 \neq 0$ and $\beta_3 z_3 \neq \beta_4 z_4$) we have

$$Q_C = \frac{1}{1 + (n_4 k_4/n_3 k_3)\exp(\beta_4 z_4 - \beta_3 z_3)VF/RT} \tag{15}$$

and

$$Q_D = \frac{1}{1 + (n_3 k_3/n_4 k_4)\exp[-(\beta_4 z_4 - \beta_3 z_3)VF/RT]} \tag{16}$$

and the ratio of coulombic yield will be

$$Q_C/Q_D = (n_3 k_3/n_4 k_4)\exp[(\beta_3 z_3 - \beta_4 z_4)VF/RT] \tag{17}$$

Equations 15–17 are of particular interest in cases where the rates of the two parallel reactions depend on potential to a slightly different extent. In such cases one would expect a slow variation of Q_C and Q_D with potential over an extended potential region.

Case 2

Here we consider a case in which the reverse reaction for one of the parallel steps is still negligible while that for the other is not (e.g., $v_{-3} = 0$; $v_{-4} \neq 0$). Step II is assumed rate-determining as before.

(a) As in Case 1a we assume first that both Steps III and IV are purely chemical

---

* The coulombic yields serve in this case as diagnostic quantities to determine the path of the reaction. A transition from Step II followed by Step III to II followed by IV is, in fact, a change in mechanism and both reaction products will only be produced in appreciable amounts in the range of potential in which a dual mechanism[5,9] occurs.

$(z_3 = z_4 = 0)$. Then

$$Q_C = \frac{v_3}{v_3 + v_4 - v_{-4}} = \frac{k_3}{k_3 + k_4 - k_{-4}[D]/[B]} \tag{18}$$

Substituting the steady state value of $[B]$ from eqn. (7) and rearranging we obtain

$$Q_C = \frac{k_3}{k_3 + k_4}\left[1 + \frac{k_{-4}[D]}{k_2[A]}\exp(-\beta_2 VF/RT)\right] \tag{19}$$

also

$$Q_D = \frac{v_4 - v_{-4}}{v_3 + v_4 - v_{-4}} = \frac{k_4 - k_{-4}[D]/[B]}{k_3 + k_4 - k_{-4}[D]/[B]} \tag{20}$$

and upon substitution from eqn. (7) we find

$$Q_D = \frac{k_4}{k_3 + k_4}\left[1 - \frac{k_3 k_{-4}[D]}{k_2 k_4[A]}\exp(-\beta_2 VF/RT)\right] \tag{21}$$

Thus the coulombic yields are dependent on potential although the rates of Steps III and IV are not directly potential-dependent.

(b) If Step III is electrochemical but Step IV is chemical (*i.e.*, $z_3 = 1$, $z_4 = 0$; $n_3 = 2$, $n_4 = 1$) we have

$$Q_C = \frac{v_3}{v_3 + (v_4 - v_{-4})/2} = \frac{k_3 \exp(\beta_3 VF/RT)}{k_3 \exp(\beta_3 VF/RT) + (k_4/2) + k_{-4}[D]/2[B]} \tag{22}$$

Substituting again the steady state value of $[B]$ from eqn. (7) and rearranging we have

$$Q_C = \frac{k_3 \exp(\beta_3 VF/RT)}{k_3 \exp(\beta_3 VF/RT) + k_4/2}\left[1 + \frac{k_{-4}[D]}{2k_2[A]}\exp(-\beta_2 VF/RT)\right] \tag{23}$$

and

$$Q_D = \frac{k_4}{k_3 \exp(\beta_3 VF/RT) + k_4/2}\left[1 - \frac{k_3 k_{-4}[D]}{k_2 k_4[A]}\exp\{(\beta_3 - \beta_2)VF/RT\}\right] \tag{24}$$

COMPARISON WITH EXPERIMENT

During the study of the mechanism of the anodic oxidation of butadiene and benzene on platinized Pt electrodes[10] the coulombic yield for CO_2 production was determined at a number of current densities. These results are shown in Figs. 1a and 2a. The corresponding partial current density, defined as the product of coulombic yield and total current density at which it is measured, is plotted in Figs. 1b and 2b as a function of potential. Figure 3 shows, for comparison, the values of the partial current densities as a function of potential calculated from eqns. (12) and (13). The similarity between Fig. 2b and Fig. 3 is rather striking if we recall that a simple three-step reaction was assumed here for the purpose of calculation, while the oxidation of benzene involves thirty charge-transfer steps and proceeds through a very complex reaction path.

CONCLUSIONS

The coulombic yield is potential-dependent in most cases over a limited potential range (0.2–0.4 V, depending on the accuracy with which it is determined) and unity
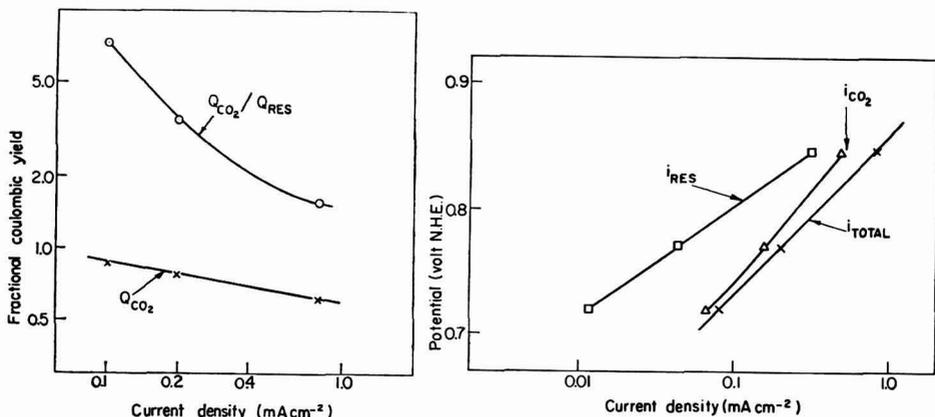
Fig. 1a. The coulombic yield for CO_2 production and the ratio of coulombic yields in the anodic oxidation of butadiene on platinized Pt electrodes as a function of current density.
Fig. 1b. Overall and partial current densities in the anodic oxidation of butadiene on platinized Pt electrodes as a function of potential.
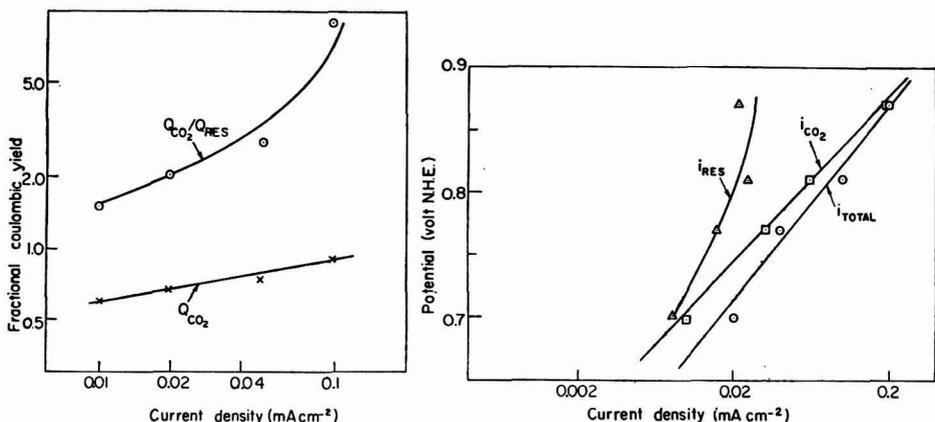
Fig. 2a. The coulombic yield for CO_2 production and the ratio of coulombic yields in the anodic oxidation of benzene on platinized Pt electrodes as a function of current density.
Fig. 2b. Overall and partial current densities in the anodic oxidation of benzene on platinized Pt electrodes as a function of potential.

outside this range. Care must be exercised in evaluating the exchange current density of a reaction when a coulombic yield of less than unity is observed. Thus the extrapolation of the observed current density to the reversible potential calculated for complete combustion of butadiene to CO_2 gives the correct exchange current density for this reaction, as can be seen from Fig. 1b. In the case of benzene, however, a similar procedure is entirely invalid (cf. Fig. 2b) since, as the reversible potential is approached, the fraction of the reaction forming CO_2 becomes exceedingly small.

In electro-organic synthesis the yield of a desired product may be increased by operating at a different potential, changing the temperature[11] or changing the concentrations of reactants in solution (cf. eqn. 19 or 23).
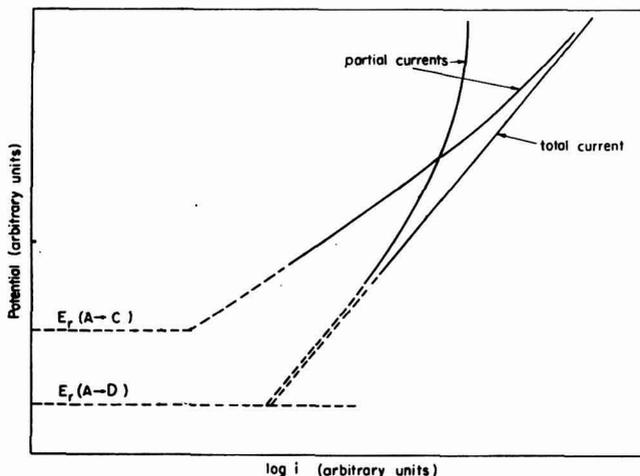
Fig. 3. Calculated partial current densities (from eqns. 12 and 13) plotted as a function of potential.

SUMMARY

The electrochemical oxidation of complex molecules (*e.g.*, hydrocarbons) sometimes involves branched reactions. Under these conditions, it is difficult to define a reversible potential and the coulombic efficiencies of product formation may then be potential-dependent.

A number of cases of the kinetics of branched reactions of the type $A \to B \overset{C}{\underset{D}{\diagdown}}$ with step $A \to B$ rate-determining, are worked out. It is found that in most cases, the coulombic yields are potential-dependent over certain potential regions. The calculated variation of coulombic yields with potential is compared with results obtained in the anodic oxidation of some unsaturated hydrocarbons.

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THE ELECTROCHEMICAL BEHAVIOR OF COPPER(II) AND COPPER(I) IONS IN A SERIES OF N,N-DIMETHYLALKYLAMIDES AND N,N-DIALKYLACETAMIDES

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INTRODUCTION

One of the most interesting features of the aqueous chemistry of copper is the inverted order of the potentials of the copper couples[1,2]. The order is not that expected for a metal for which the second ionization potential is greater than the first:

$$Cu^{2+} + e = Cu^+; \quad E° = -0.089 \ V \ vs. \ S.C.E.$$

$$Cu^+ + e = Cu \ ; \quad E° = +0.279 \ V \ vs. \ S.C.E.$$
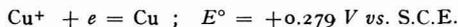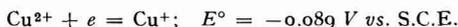
Because of this order of the potentials of the two couples, copper(II) ion in water is reduced in one step at the dropping mercury electrode and copper(I) ion is unstable, disproportionating to give copper(II) ion and metallic copper. By the use of appropriate non-aqueous solvents in which the solvation energy of copper(I) ion is higher than in water and/or in which the solvation energy of copper(II) ion is lower than in water, the order of the potentials, however, can be reversed[3], enabling copper(II) ion to be reduced in two steps and stable copper(I) solutions to be prepared. The solvation energy of copper(II) ion is very sensitive to slight changes in the basicity of the solvent. Even in the series of solvents: water, methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, 2-butanol, 2-methyl-1-propanol, and 3-pentanol, there is a pronounced change in the solvation energy of copper(II) ion, as indicated by the change in the potential of the copper(II)–copper(I) couple[3,4,5]. On the other hand, in this series of solvents the solvation energy of copper(I) ion changes very little and the potential of the copper(I)–copper couple is fairly constant. The decrease in solvation energy of copper(II) ion in these alcohols, surprisingly, is large enough that solutions of copper(I) ion are stable with respect to disproportionation.

In some preliminary studies on the stability of copper(I) ion in non-aqueous solvents we noted with interest that in dimethylformamide, as in water, copper(II) ion is reduced in one step at the dropping mercury electrode, with a value of +0.04 V *vs.* S.C.E. for the half-wave potential, a value practically identical with that for the same process in water (+0.03 V *vs.* S.C.E.). The similarity of the half-wave potentials in the two solvents suggests that the basicity of dimethylformamide with respect to copper(II) ion is almost identical with that of water. In addition, the one-step re-

duction process strongly suggests that the order of the potentials of the copper couples in dimethylformamide is inverted, as in water.

This paper deals with the results of an electrochemical investigation to determine (i) whether the order of the potentials of the copper couples in dimethylformamide and other similar amides is inverted, as in water, and (ii) the effect of modification of the solvent, dimethylformamide, (by substitution of alkyl groups for the formyl hydrogen and N-methyls) on the electrochemical behavior of copper(II) ion brought about by changes in the solvation energy of copper ions. Also considered in this study is the change in the solvation energy of copper ions in the series of amides studied, compared to that found in the lower alcohols. The following amides were examined: N,N-dimethylformamide, N,N-dimethylacetamide, N,N-dimethylpropionamide, N,N-dimethylbutyramide, N,N-diethylacetamide, N,N-diisopropylacetamide, N,N-dibutylacetamide, and N,N-diisopropylpropionamide.

EXPERIMENTAL

The volumetric equipment and technique used in this study have been described previously[6,7]. All amides, except for dimethylformamide, were Eastman white-label material fractionally distilled at reduced pressure. Only the middle fraction distilling at a constant temperature was collected and used. N,N-dimethylpropionamide, N,N-dimethylbutyramide, and N,N-diisopropylpropionamide were treated with a small amount of phthalic anhydride before distillation[8]. Fisher Certified Reagent-grade N,N-dimethylformamide was purified by distillation at reduced pressure; the middle fraction distilling at a constant temperature was collected and used. Lithium perchlorate and hexa-aquo-copper(II) perchlorate (G.F . Smith Chemical Co.) were dried in a vacuum oven at 70° for 48 h. Background scans of 0.1 M lithium perchlorate solutions with a dropping mercury electrode and a rotating platinum electrode gave no evidence for the presence of choride ion or other oxidizable or reducible impurities. Solutions of copper(I) were prepared by diluting 0.05–0.5 ml of a solution of copper(I) perchlorate in nitromethane to 10 ml with amide. Care must be excercised in this dilution operation to prevent air oxidation of copper(I) ion. The presence of the small amounts of nitromethane had no effect on the current–voltage curves. Solutions of copper(I) in nitromethane were obtained by shaking carefully de-aerated copper(II) perchlorate solutions with freshly cleaned pieces of copper metal for *ca.* 20 min.

The water content of the amide solutions was determined by the Karl Fischer method. The following values were obtained for 0.1 M lithium perchlorate solutions: $3 \cdot 10^{-3}$ M for dimethylformamide; $1 \cdot 10^{-2}$ M for diisopropylacetamide; $2 \cdot 10^{-2}$ M for diethylacetamide and for diisopropylpropionamide; $4 \cdot 10^{-2}$ M for dimethylacetamide, for dimethylpropionamide, and for dimethylbutyramide.

RESULTS

A summary of the pertinent results is presented in Table 1. These results were obtained with solutions of copper(I) ion. Because of the closeness of the potentials of the two copper couples to each other, the polarograms were all single-wave, anodic–cathodic current–voltage curves, except for dimethylpropionamide and diisopropylpropionamide solutions. $E^{\circ\prime}_{Cu(II),Cu(I)}$ and $E^{\circ\prime}_{Cu(I),Cu(Hg)}$ for all the amides except these two, therefore, were evaluated from the anodic and cathodic portions of the single-wave polarograms

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TABLE 1

SUMMARY OF ELECTROCHEMICAL DATA ON THE BEHAVIOR OF COPPER(I) ION IN SOME SELECTED
SUBSTITUTED AMIDES[a, b, c]

Solvent	Elec-trode	Electrode reaction $Cu(I) \rightarrow Cu(II)$		Electrode reaction $Cu(I) \rightarrow Cu$ or $Cu(Hg)$	
		$E^{\circ\prime}{}_{Cu(II),Cu(I)}$	$0.059/n$	$E^{\circ\prime}{}_{Cu(I),Cu}$	$0.059/n$
N,N-Dimethylformamide	Pt	+0.04	0.090	0.00	0.27
	Hg	+0.05[d]	(0.065)[e]	0.00[d]	(0.065)[e]
N,N-Dimethylacetamide	Pt	+0.16	0.085	+0.07	0.065
	Hg	+0.14[d]	(0.094)[e]	+0.05[d]	(0.094)[e]
N,N-Diethylacetamide	Pt	+0.17	0.067	+0.07	0.057
	Hg	+0.12[d]	(0.094)[e]	+0.02[d]	(0.094)[e]
N,N-Diisopropylacetamide	Pt	+0.24	0.10	+0.02	0.060
	Hg	+0.12[d]	(0.10)[e]	+0.02[d]	(0.10)[e]
N,N-Dibutylacetamide	Pt	+0.31	0.19	+0.07	0.14
	Hg	+0.16[d]	(0.096)[e]	+0.07[d]	(0.096)[e]
N,N-Dimethylpropionamide	Pt	+0.31	0.065	+0.11	0.059
	Hg	+0.11	0.091	−0.08	0.050
N,N-Dimethylbutyramide	Pt	+0.29	0.053	+0.11	0.058
	Hg	+0.19[d]	(0.13)[e]	+0.06[d]	(0.13)[e]
N,N-Diisopropylpropionamide	Pt	+0.33	0.079	+0.06	0.094
	Hg	+0.13	0.094	−0.03	0.086

[a] All solutions are 0.1 M in $LiClO_4$ and $1 \cdot 10^{-4}$–$8 \cdot 10^{-4}$ M in Cu(I).   [b] All $E^{\circ\prime}$ and $0.059/n$ values
are the average of two or more runs.   [c] Each $E^{\circ\prime}$ value has been corrected for junction potential
difference between the solvent system $vs.$ S.C.E. and the dimethylformamide solution $vs.$ S.C.E.,
(see RESULTS).   [d] Value for anodic or cathodic part of a single anodic–cathodic wave.   [e] Value
for the single anodic–cathodic wave.

With the exception of the results for dimethylformamide ($E^{\circ\prime}{}_{Cu(II),Cu(I)}$ = +0.03 V,
$0.059/n$ = 0.093; $E^{\circ\prime}{}_{Cu(I),Cu}$ = −0.01 V, $0.059/n$ = 0.14) and dimethylacetamide
($E^{\circ\prime}{}_{Cu(II),Cu(I)}$ = +0.13 V, $0.059/n$ = 0.093; $E^{\circ\prime}{}_{Cu(I),Cu}$ = +0.03 V, $0.059/n$ = 0.090)
solutions, the rotating platinum electrode data obtained with copper(II) solutions
were not in agreement with those obtained with copper(I) solutions. The current–
voltage curves for the copper(II) solutions in these cases were ill-defined, drawn-
out and/or shifted in the negative direction.

In all the amides, except diisopropylpropionamide, the reduction of copper(II) ion
ion to the metal at the dropping mercury electrode takes place in one step. For di-
isopropylpropionamide solution, a two-step wave with potentials ($E^{\circ\prime}{}_{Cu(II),Cu(I)}$ =
+0.17 V, $0.059/n$ = 0.089; $E^{\circ\prime}{}_{Cu(I),Cu(Hg)}$ = −0.03 V, $0.059/n$ = 0.067) in good
agreement with those obtained with the dropping mercury electrode and copper(I)
solutions was observed. In dimethylformamide ($E^{\circ\prime}{}_{Cu(II),Cu(Hg)}$ = +0.04 V, $0.059/n$=
0.040), dimethylbutyramide ($E^{\circ\prime}{}_{Cu(II),Cu(Hg)}$ = +0.10 V, $0.059/n$ = 0.12), and di-
isopropylacetamide ($E^{\circ\prime}{}_{Cu(II),Cu(Hg)}$ = +0.07 V, $0.059/n$ = 0.11), the half-wave po-
tential agrees with the potentials for the copper(II)–copper(I) and copper(I)–copper-
amalgam couples obtained with copper(I) solutions. The value for $E^{\circ\prime}{}_{Cu(II),Cu(Hg)}$ in

each of the other solvents, however, is 0.06–0.15 V more negative than that expected
from the values for $E^{\circ\prime}$ for the two copper couples obtained from copper(I) solutions.
In addition, the values in these solvents are not in line with the $E^{\circ\prime}$ values for the
two copper couples obtained from copper(I) solutions with the rotating platinum
electrode.

Differences in liquid-junction potential among the solvents were eliminated by
adding the following value to each potential[9], $E_{corr.} = E_{\frac{1}{2}(oxid.\ of\ tris\ (4,7-dimethyl-1,10-phenanthroline)iron(II)}$ (dimethylformamide) $- E_{\frac{1}{2}(oxid.\ of\ tris\ (4,7-dimethyl-1,10-phenanthroline)iron(II)}$ (solvent).

Dimethylformamide was selected as the reference solvent. The half-wave potentials
for the oxidation of tris(4,7-dimethyl-1,10-phenanthroline)iron(II) in the various
amides are: dimethylformamide, +0.93 V; dimethylacetamide, +0.97 V; diethyl-
acetamide, +1.03 V; dibutylacetamide, +0.99 V; diisopropylacetamide, +1.05 V;
dimethylpropionamide, +0.99 V; dimethylbutyramide, +1.00 V; and diisopropyl-
propionamide, +1.08 V.

DISCUSSION

The values for $0.059/n$ in Table 1 indicate that, except in only a few cases, the electrode
reactions Cu(I) → Cu(II) and Cu(I) → Cu are essentially reversible. The effect of substitu-
tion of alkyl groups for the formyl hydrogen and for the N-methyl groups in dimethyl-
formamide, on the ability of the resulting amides to solvate copper(II) and copper(I)
ions can therefore be evaluated by the use of the $E^{\circ\prime}$ values. In those few cases where
the value of $0.059/n$ indicates an irreversible electrode process for the copper(II)–
copper(I) step, single copper(II), copper(I) waves which pass through zero current
were, however, obtained for solutions containing both copper(II) and copper(I) ions,
indicating that the deviation of the $0.059/n$ value from the theoretical value is the
result of electrode surface effects rather than an irreversible electrode process. In
addition, the elimination of differences in liquid-junction potential among the solvents
by the use of the half-wave potential for the oxidation of tris(4,7-dimethyl-1,10-
phenanthroline)iron(II) makes possible a meaningful analysis of the electrochemical
data.

The values for $E^{\circ\prime}_{Cu(II),Cu(I)}$ and $E^{\circ\prime}_{Cu(I),Cu(Hg)}$ evaluated from the single-step
anodic–cathodic polarograms for copper(I) solutions are undoubtedly close to the
true values for the two redox couples; only when the anodic–cathodic polarogram
is a split wave, as in dimethylpropionamide and in diisopropylpropionamide, are the
values for $E^{\circ\prime}$ the true values. The values for $E^{\circ\prime}$ obtained with the dropping mercury
electrode, therefore, will not be utilized to discuss the relative differences in solvation
energy of copper ions in the amides. Moreover, the reason for the more-negative-than-
expected values for $E^{\circ\prime}$ of both copper couples in dimethylpropionamide and in di-
isopropylpropionamide evaluated from the anodic–cathodic polarograms for copper(I)
solutions is not fully understood.

Correction for the liquid-junction potential difference between 0.1 M LiClO$_4$ (aq.)
vs. S.C.E. (aq.) and 0.1 M LiClO$_4$ (dimethylformamide) vs. S.C.E. (aq.)[9] gives the
following values for the potentials of the copper couples in water based on dimethyl-
formamide as the reference solvent: $E^{\circ\prime}_{Cu(II),Cu} = +0.20$ V; $E^{\circ\prime}_{Cu(II),Cu(I)} = +0.01$ V,
$E^{\circ\prime}_{Cu(I),Cu} = +0.38$ V[3]. These potentials indicate that the principal reason for
the normal order of the potentials of the copper couples in the amides as compared

to the inverted order in water is that the solvation energy of copper(I) ion in the amides is larger than in water. Although the solvation energy of copper(II) ion in the lower amides also is larger than in water (by *ca.* 0.4 V in the case of dimethyl-formamide), as it is evident, the difference is not large enough relative to the difference in solvation energy of copper(I) ion to give rise to an inverted situation with regard to the order of the potentials of the copper couples.

The behavior of copper ions in dimethylformamide, originally thought to be similar to that of copper ions in water on the basis of the one-step reduction step for copper(II) ion at the dropping mercury electrode at a potential very close to that in water, is more like that of copper ions in methanol than in water. The potentials of the copper couples in methanol ($E^{\circ\prime}_{Cu(II),Cu(I)} = +0.25$ V *vs.* S.C.E. and $E^{\circ\prime}_{Cu(I),Cu} = +0.19$ V *vs.* S.C.E.) are in the normal order and differ by 0.06 V. These values for $E^{\circ\prime}$ indicate that the solvation energy of copper(I) and of copper(II) ions in methanol, however, is less than in dimethylformamide by *ca.* 0.2 V [copper(I)] and by *ca.* 0.4 V [copper(II) ion].

Infrared spectral data of the compound, copper(II) sulfate–4-dimethylacetamide–water[10], and of nickel(II)– and chromium(III)–amide complexes[11] indicate through decrease in the C=O stretching frequency that co-ordination of amides to copper(II) ion occurs through the oxygen atom rather than the nitrogen[12]. No spectral data are available on copper(I)–amide complexes. However, because (i) the infrared spectrum for AgClO$_4$–dimethylacetamide–water[10] indicates co-ordination of dimethylacetamide to silver(I) ion through the oxygen atom and (ii) the properties of many copper(I) compounds are similar to those of the corresponding silver(I) compounds, it is likely that copper(I) is also solvated by amides through the oxygen site.

As in the alcohols, the potentials for the copper(I)–copper couple in the amides indicate that there is very little change in the solvation energy of copper(I) ion from the simplest (dimethylformamide) to the most heavily substituted (diisopropylpropionamide) amide examined. Consequently, in these two solvent systems, copper(I) ion has probably two solvent molecules bound to it in a linear arrangement. If the alcohol and amide molecules are bound to copper(I) ion in a tetrahedral arrangement, pronounced changes in the solvation energy of copper(I) ion and in the potential of the copper(I)–copper couple as a result of steric effects would have been observed. The square planar or distorted octahedral arrangement of amides and of alcohols about the copper(II) ion accounts (because of considerable steric interaction among the solvent molecules in the co-ordination sphere) for the pronounced change in solvation energy of copper(II) ion in the alcohols and amides and in the potential of the copper(II)–copper(I) couple. It is of interest to note that the decrease in solvation energy of copper(II) ion in the amides, from dimethylformamide to diisopropylpropionamide, is practically identical with that in the alcohols, from methanol to the butanols. Because of the replacement of the formyl hydrogen and two N-methyl groups with three large alkyl groups, a greater change in the solvation energy of copper(II) ion would be expected with the amides than with the alcohols. The noticeably smaller change in the solvation energy of the copper(II) ion in the amides than that expected is due to the fact that the oxygen atom in the amides is in a less sterically affectible position than the oxygen in the alcohols. Finally, the copper(II)–copper(I) potentials indicate that the solvating ability of amides is more sensitive to changes in the carbon-chain length of the alkyl group attached to the carbonyl

carbon than of the alkyl groups attached to the nitrogen.

Because no information is available on the ion-pair formation constants of Li^+, ClO_4^-; Cu^+, ClO_4^-; and Cu^{2+}, ClO_4^- in the amides studied or of the dielectric constants of the amides, no definite statement can be made with regard to the effect of ion-pair formation on the chemistry of copper ions in the amides. The constancy of $E^{\circ\prime}_{Cu(I),Cu}$ and the change of $E^{\circ\prime}_{Cu(II),Cu(I)}$ in the expected manner, however, suggest that the extent of ion-pairing is remarkably small.

SUMMARY

The electrochemical behavior of copper ions has been investigated in N,N-dimethyl-formamide, N,N-dimethylacetamide, N,N-diethylacetamide, N,N-diisopropylacet-amide, N,N-dibutylacetamide, N,N-dimethylpropionamide, N,N-dimethylbutyra-mide, and N,N-diisopropylpropionamide. The potentials of the two copper couples in these amides are in the normal order, and copper(I) solutions, as a result, are stable with respect to disproportionation. Except for the fact that the potentials of the copper(II)–copper(I) and copper(I)–copper(o) couples are slightly more negative than in the lower alcohols because of the slightly higher solvation energy of copper(II) and copper-(I) ions in amides than in alcohols, the electrochemical behavior of copper ions in amides is very similar to that in the lower alcohols. Changes in the carbon-chain length of the alkyl group attached to the carbonyl carbon appear to have a greater effect on the solvation energy of copper(II) ion in amides than changes in the carbon-chain length of the alkyl groups attached to the nitrogen.

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A POTENTIOMETRIC STUDY OF THE REACTION BETWEEN V$_2$O$_5$ AND MOLTEN KNO$_3$

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INTRODUCTION

According to a procedure described by NORBLAD[1], potassium metavanadate can be prepared by fusing V$_2$O$_5$ with KNO$_3$. This is, however, not in agreement with the newly established fact that metavanadate in this melt behaves as a strong Lux-acid[2] which immediately takes its primary oxide ion from the nitrate base-electrolyte to yield pyrovanadate[3]:

$$2 \text{ VO}_3^- + 2 \text{ NO}_3^- = \text{V}_2\text{O}_7{}^{4-} + \text{N}_2\text{O}_5 \tag{1}$$

The reaction between V$_2$O$_5$ and molten KNO$_3$ was studied, therefore, in detail. The technique used was that of the *in situ* potentiometric acid–base titration recently developed in our laboratory[3-6]. V$_2$O$_5$–KNO$_3$ melts of different compositions were titrated with Na$_2$O$_2$. An oxygen (Pt) electrode was applied as indicator electrode and an Ag/Ag(I)/glass electrode acted as reference[3,4]. The titrations were conducted under a wide variety of conditions. The following experimental parameters were varied: concentration of V$_2$O$_5$, fusion time, fusion temperature and the addition of NaVO$_3$ and Na$_4$V$_2$O$_7$ at different stages of neutralization. From these experiments it was established that the reaction of the pentoxide with molten KNO$_3$ is not as simple as claimed by NORBLAD[1]. The pentoxide reacts first with the nitrate base-electrolyte to yield KVO$_3$ which quickly attacks the nitrate to give both pyrovanadate and a nitrate complex of the probable formula [VO$_3$–O–NO$_2$]$^{2-}$. The kinetics of the reaction has been studied in some detail and a mechanism accounting for the disappearance of the pentoxide is proposed.

EXPERIMENTAL

The technique for potentiometric acid–base titration in fused salts has been previously described[4,5]. An oxygen (Pt) electrode was used as indicator electrode. The reference half-cell was a silver wire dipping into a AgNO$_3$–KNO$_3$ melt (2.04% AgNO$_3$, w/w) and separated from the main melt by a solid Pyrex glass tube[3]. All chemicals (A.R. quality) were used without further purification. Both the yellow and brown forms of V$_2$O$_5$ were applied without any apparent difference in behaviour. Na$_2$O$_2$ was the titrant and its thermal decomposition in the melt introduced the desired quantity of oxide ion. 50.000 g of dry KNO$_3$[5] was used as a medium for titration.

At the start of an experiment, a weighed quantity of V$_2$O$_5$ was added to the nitrate

melt and a definite time was allowed to elapse before the titration was started. In kinetic experiments this time is referred to as *the reaction time*. The titration proper was of relatively shorter duration and a correction for this period was not considered. Unless otherwise stated, all experiments were performed at 350°.

RESULTS AND DISCUSSION

After a definite reaction time (*e.g.*, 210 min), the titration curves of V_2O_5–KNO_3 melts show three distinct neutralization steps similar to those of Fig. 1. Along step I, which occurs at the most positive potentials, the reddish-brown suspension of the
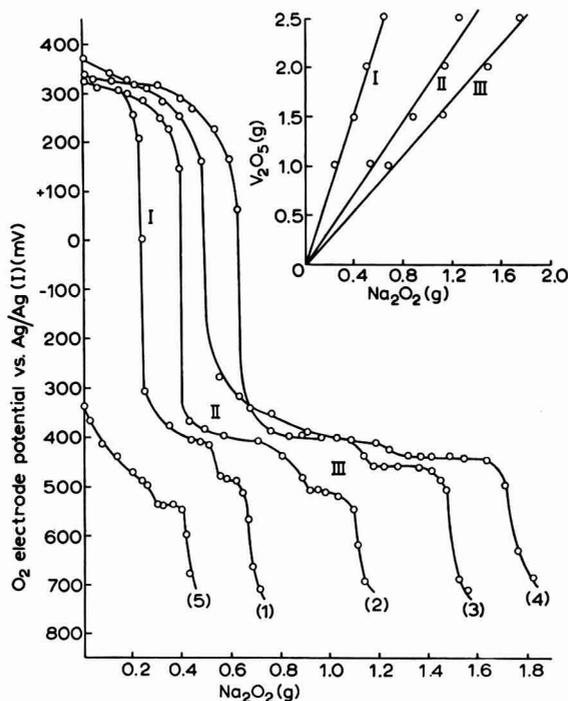
Fig. 1. Potentiometric titration curves of V_2O_5–KNO_3 melts at 350°. (1), 1.000 g; (2), 1.500 g; (3), 2.000 g; (4), 2.500 g V_2O_5/50.000 g KNO_3. (5), 1.000 g V_2O_5 after elimination of step I. Insert: relationship between the quantities of V_2O_5 and Na_2O_2 consumed at the inflexion points.

pentoxide gradually disappears and the melt becomes clear. As will be shown later, this step represents the conversion of V_2O_5 into metavanadate according to

$$V_2O_5 + O^{2-} = 2 VO_3^-$$ (2)

Step II occurs at potentials characteristic for the transformation of pyrovanadate into orthovanadate. This, together with the fact that this step increases in length upon adding extra metavanadate or pyrovanadate to the melt (see later), justifies the conclusion that the reaction taking place during this stage is

$$V_2O_7^{4-} + O^{2-} = 2 VO_4^{3-}$$ (3)

Theoretical analysis of these parts of the curves, following the procedure presented earlier[3] also confirms this conclusion.

The characterization of step III-acid will be discussed in a later part of this paper. It should be clear at this point, however, that this step is due to the neutralization of a new acid which does not result from the stepwise reaction of pyrovanadate because the neutralization of the latter acid occurs in a single step[3]. The reaction of step III-acid with O^{2-} similarly leads to the formation of the most basic salt of vanadium(V), *viz.*, the orthovanadate. The quantity of Na_2O_2 consumed at the inflexion point of any of the three neutralization steps is proportional to the V_2O_5 content of the melt provided that the other reaction parameters (temperature, reaction time, quantity of KNO_3) are held constant (see insert of Fig. 1).

For any one value of V_2O_5 content in the melt (1 g/50.00 g KNO_3) an increase in the reaction time leads to a corresponding decrease in the consumption of Na_2O_2 along step I (Fig. 2). The decrease increases with increase in temperature. Complete
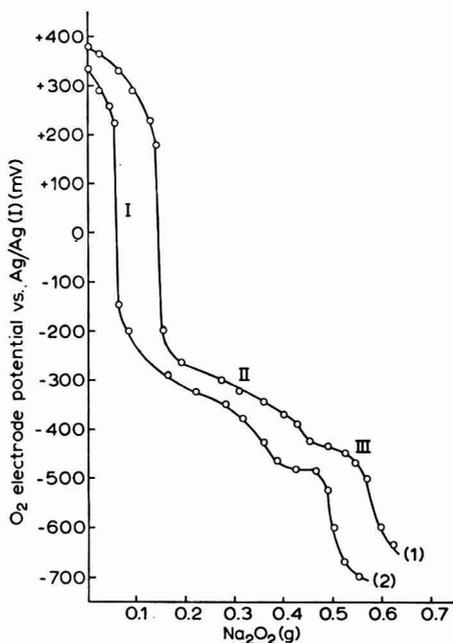
Fig. 2. Effect of the fusion time on the titration curves of 1.000 g V_2O_5/50.000 g KNO_3. (1), 1 h; (2), 4 h. Temp. 390°.

elimination of the first neutralization step can therefore be effected by allowing the reaction to proceed for a long enough period and is accelerated by raising the temperature. Under these conditions the neutralization curves show steps II and III clearly (Fig. 1, curve 5). The quantities of Na_2O_2 consumed along these two steps are independent of the reaction time.

From the quantities of Na_2O_2 consumed along step I, the corresponding molarities of the V_2O_5 remaining at the start of titration are calculated. When these are plotted as a function of the reaction time, the lines of Fig. 3 are obtained. It can be seen from these lines that, the concentration of V_2O_5 varies linearly with time. Also, the time for one half of the pentoxide to react with the nitrate is proportional to the initial

concentration of V_2O_5. Thus, for example, in two nitrate melts containing 0.5000 and 1.000 g V_2O_5/50.000 g KNO_3 at 350°, half the quantity of the pentoxide disappeared in 192 and 380 min, respectively. These figures indicate that the reaction of V_2O_5 with molten KNO_3 is zero-order with respect to V_2O_5. From the curves of Fig. 3 the rate constant of the reaction at 350, 390 and 425° are computed to be 5.60×10^{-5}, 2.35×10^{-4} and 1.00×10^{-3} mole $l^{-1}min^{-1}$ respectively. A plot of the logarithm of these constants as a function of $1/T$ gives a straight line; its slope gives the activation energy of the reaction as 32.4 kcal/mole.
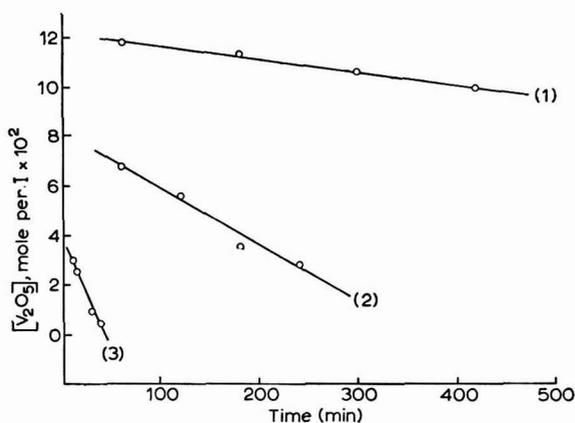
Fig. 3. Disappearance of V_2O_5 as a function of fusion time and temperature. (1), 350°; (2), 390°; (3), 425°.

Since step II of the neutralization curves represents the transformation of pyro-vanadate into orthovanadate, the overall reaction between V_2O_5 and KNO_3 can be represented as

$$V_2O_5 + 4\ NO_3^- = V_2O_7^{4-} + 2\ N_2O_5 \tag{4}$$
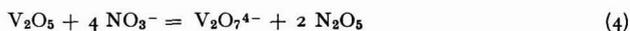
It is unlikely that four nitrate ions react simultaneously with one molecule of V_2O_5. One is bound to assume, therefore, that reaction (4) occurs in a stepwise fashion. Acid–base transformations involving nitrate ion are said to occur through the breaking of the $N-O^-$ bond of the nitrate ion and the formation of a positively charged nitronium ion, NO_2^+ (ref. 7). Applying this principle to the reaction under consideration, one can write

$$V_2O_5 + NO_3^- = 2\ VO_3^- + NO_2^+ \tag{5}$$

$$2\ VO_3^- + NO_3^- = V_2O_7^{4-} + NO_2^+ \tag{6}$$

$$2\ NO_2^+ + 2\ NO_3^- = 2\ N_2O_5 \tag{7}$$
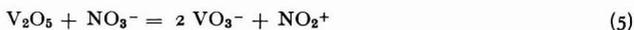
Reaction (7) cannot be rate-determining since it involves the combination of oppositely-charged ions. Similarly, the reaction between metavanadate and nitrate proceeds at a much higher rate than that of the disappearance of V_2O_5 (see later). It is suggested, therefore, that step (5) is the rate-determining process in the reaction between V_2O_5 and molten KNO_3. The following experiment supports this conclusion: to 50.000 g of fused KNO_3 a mixture of solid V_2O_5 (1 g) and enough Na_2O_2 to transfer

the pentoxide into metavanadate (0.430 g) was added. The potential of the oxygen electrode dropped directly to values characteristic for $V_2O_7^{4-}$ and the red colour of the melt was instantaneously discharged. Since reaction (6) is fast, such behaviour can be explained only on the basis that (5) has been accelerated by the presence of free oxide ion. The first neutralization step of Figs. 1 and 2 represents, therefore, the transformation of V_2O_5 into VO_3^-. The molarities of V_2O_5 drawn on Fig. 3 are calculated on this basis. It is of interest to remark here that further neutralization of the reaction product of the experiment described above showed steps II and III distinctly. That step III is recorded is remarkable since V_2O_5 had, under the given experimental conditions, little time to react with the nitrate base-electrolyte. The formation of the acid of step III must, therefore, be related to the momentarily formed VO_3^-. Evidence for this conclusion will be given later.

Metavanadate which results from the interaction of V_2O_5 with nitrate (or O^{2-}) does not exist as such in the melt. Being a strong Lux-acid, it directly attacks the nitrate base-electrolyte to yield pyrovanadate (or its equivalent)[3]. This conclusion is supported by the results of the present investigation. Thus, for one mole of V_2O_5 to transform into the most basic vanadate, the ortho-vanadate, three equivalents of oxide ion are required according to

$$V_2O_5 + O^{2-} = 2 \ VO_3^- \tag{8}$$

$$2 \ VO_3^- + O^{2-} = [V_2O_7^{4-}] \tag{9}$$

$$[V_2O_7^{4-}] + O^{2-} = 2 \ VO_4^{3-} \tag{10}$$

where $[V_2O_7^{4-}]$ denotes pyrovanadate or its equivalent. In the experiments of Figs. 1 and 2 (and the like), the consumption of O^{2-} (calculated in terms of Na_2O_2) is always less than two equivalents per mole of V_2O_5. When step I is completely eliminated (by fusing for a long time or by the addition of enough Na_2O_2), steps II and III together consume exactly one equivalent of O^{2-} corresponding to reaction (10). Apparently the remaining two equivalents of O^{2-} are gained from the nitrate base-electrolyte. Thus, metavanadate cannot exist in nitrate melts.

It is of interest to observe that the addition of solid V_2O_5 (1 g) together with two equivalents of Na_2O_2 (0.86 g) to fused KNO_3 results in the direct formation of ortho-vanadate, VO_4^{3-}. This has been ascertained both from measurement of the potential of the oxygen electrode and from the fact that further neutralization with Na_2O_2 affords no evidence of the presence of any titrable vanadate in the melt. From what has been presented above, we know that one free oxide ion is consumed in reaction (8). Since, on the other hand, reaction (10) cannot take place except through a free oxide ion ($[V_2O_7^{4-}]$ is stable in nitrate melts), one is bound to conclude that reaction (9) obtains its oxide ion from the nitrate ground-electrolyte. This is strange in view of the fact that during the time reaction (9) is taking place *via* the nitrate ion, *free* oxide ion is available in the melt.

To complement the experiments described above, the behaviour of metavanadate under similar conditions was studied. $NaVO_3$ reacts with fused KNO_3 to yield pyro-vanadate which is stable and can be quantitatively titrated with Na_2O_2. When, however, $NaVO_3$ is added to a nitrate melt containing enough Na_2O_2 to transform it into pyrovanadate, direct transformation into orthovanadate takes place. Had the metavanadate reacted with the free oxide ion, the resulting pyrovanadate would

have remained as such in the melt. This, however, is not the case. Such a result again indicates that VO_3^- reacts first with the nitrate to yield the pyro-salt and that the latter consumes the free oxide ion in its change to orthovanadate. This is an odd kind of mechanism. Thus, whereas Na_2O_2 in nitrate melts is almost completely ionized[8], and the oxide-ion activity of pure KNO_3 — as inferred from the equilibrium potential of the oxygen electrode[8] — amounts to only ca. 10^{-7} mole l^{-1}, metavanadate reacts preferentially with the nitrate and not with the free oxide ion, despite the fact that the former reaction involves the cleavage of the $N–O^-$ bond. Oxide-ion transfer between the nitrate and metavanadate appears, therefore, to be more complex than represented by the overall reaction (1). The process most probably involves the primary formation of an intermediate complex which yields pyrovanadate upon decomposition. Because of the high concentration of the nitrate ion relative to the free oxide ion, probability of direct reaction with free oxide ion is low.

In order to understand the mechanism by which $NaVO_3$ reacts with fused KNO_3, the variation of the potential of the oxygen electrode with time, after adding the acid to the melt, was followed. For a strong acid like metavanadate, one would expect the equilibrium potential of $V_2O_7^{4-}$ to be attained from positive values. If, on the other hand, the reaction with nitrate is exceedingly fast, the equilibrium potential would be established instantaneously. The actual behaviour is, however, neither of the two described above. As is seen from Fig. 4, curve 1, the potential of the oxygen electrode
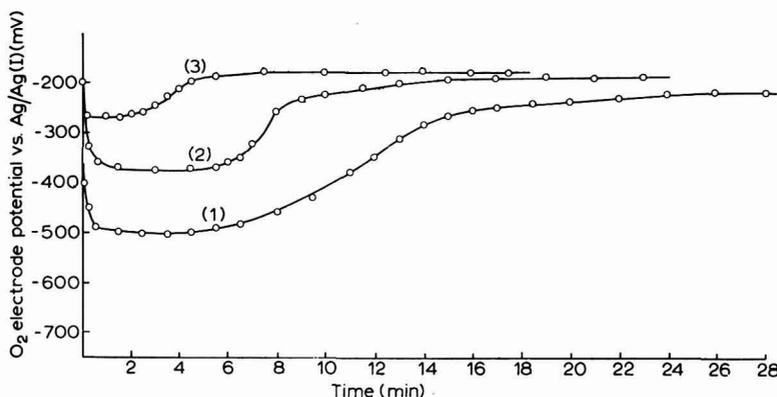
Fig. 4. Variation of the oxygen electrode potential after the addition of 1-g quantities of $NaVO_3$ to KNO_3 melts at 350°.

first dropped to values intermediate between those for $V_2O_7^{4-}$ and VO_4^{3-}. After a limited interval, the potential levelled up again to that for $V_2O_7^{4-}$ after which it remained constant. The addition of metavanadate to the same melt (each addition, 1 g) produced the same effect but to a lesser extent. The titration of the melts thus obtained, showed only a single step, corresponding to pyrovanadate. The negative potentials measured at the moment of addition of $NaVO_3$ to the nitrate melt strongly support the idea of formation of a reaction product more basic than $V_2O_7^{4-}$. The levelling up of the potential and the fact that only pyrovanadate was detected in the melt can be explained on the premise that the basic compound underwent a process of rearrangement to yield the pyro-salt.

The effect of adding extra $NaVO_3$ and $Na_4V_2O_7$ to V_2O_5–KNO_3 melts was investigated in order to gain some knowledge about the conditions leading to the formation of the acid of step III.

In Table 1a are given the quantities of Na_2O_2, in mg, consumed along the different neutralization steps of 1 g of V_2O_5 and also by various amounts of $NaVO_3$ and of $Na_4V_2O_7$. In Tables 1b and 1c the corresponding quantities for mixtures of 1 g of V_2O_5 and increasing quantities of $NaVO_3$ are presented. In series 1c the first neutralization step of the V_2O_5 curves was completely eliminated by adding the necessary

TABLE 1

QUANTITIES OF Na_2O_2 CONSUMED ALONG THE TITRATION STEPS OF V_2O_5, $NaVO_3$ AND $Na_4V_2O_7$, (temperature 350°, fusion time 75 min)

	Acid (g)			Na_2O_2 (mg)			
	V_2O_5	$NaVO_3$	$Na_4V_2O_7$	Step I	Step II	Step III	III/II
(a)	1.0	—	—	245	310	145	0.48
	—	0.5	—	—	160	—	—
	—	1.0	—	—	320	—	—
	—	1.5	—	—	480	—	—
	—	2.0	—	—	640	—	—
	—	—	0.5	—	127	—	—
	—	—	1.0	—	255	—	—
(b)	1.0	0.5	—	320	440	180	0.41
	1.0	1.0	—	320	490	310	0.63
	1.0	1.5	—	310	660	295	0.45
	1.0	2.0	—	280	670	430	0.64
(c)	1.0	—	—	—	290	130	0.45
	1.0	0.5	—	—	375	205	0.55
	1.0	1.0	—	—	475	265	0.56
	1.0	1.5	—	—	545	365	0.67
(d)	1.0	—	0.5	225	350	210	0.59
	1.0	—	1.0	90	420	240	0.57

amount of Na_2O_2 before introducing the metavanadate into the melt. The data for V_2O_5–$Na_4V_2O_7$–KNO_3 melts are given in Table 1d. The experiments were conducted at 350° and the fusion time was 75 min.

As can be seen from the figures of Table 1b, the addition of $NaVO_3$ to V_2O_5–KNO_3 melts resulted in a slight increase in the quantity of Na_2O_2 consumed along step I. Although this increase is a little above our accepted margin for the reproducibility of results ($\pm$ 20 mg), the fact that this increase is practically independent of the amount of $NaVO_3$ justifies our conclusion that metavanadate does not affect the first neutralization step.

Steps II and III are, however, affected by the addition of $NaVO_3$. Thus, for example, a 1-g quantity of V_2O_5 consumes 310 and 145 mg of Na_2O_2 along Steps II and III, respectively. As has already been pointed out, the two quantities together represent one third of the amount of Na_2O_2 necessary to transfer V_2O_5 into VO_4^{3-}. On the other hand, 1 g of $NaVO_3$ in KNO_3 (actually present as pyrovanadate) consumes 320 mg Na_2O_2 at potentials corresponding to step II. If V_2O_5 and $NaVO_3$ react independently, one would expect step II to consume 630 mg and step III to remain unaffected.

Experiments showed, however, that steps II and III consumed, respectively, 490 and 310 mg Na_2O_2. The increase in Na_2O_2 consumption along step III practically accounts for VO_3^- not present in the form of $V_2O_7^{4-}$. The relevant data for mixtures with other V_2O_5/VO_3^- ratios are given in Table 1b.

Almost the same results were obtained with V_2O_5–KNO_3 melts in which the neutralization step I was eliminated by the addition of Na_2O_2 before $NaVO_3$ was added (Table 1c). Here, also, an increase in the consumption of sodium peroxide along step III was recorded. This clearly shows that the acid of this step results from the interaction of VO_3^- with the melt.

Because of the more negative potentials of step III with respect to those for the $V_2O_7^{4-}$ step, it was thought at first that the acid of step III was more basic than $V_2O_7^{4-}$ (in the sense of a higher O:V ratio). If this was the case, the acid would require, in its transformation into orthovanadate, an amount of O^{2-} less than that needed by an equivalent quantity of $V_2O_7^{4-}$. Experimentally it is well established, however, that steps II and III of V_2O_5 curves, as well as the increase in both steps upon adding VO_3^-, consume one equivalent of O^{2-} corresponding to reaction (10). It seems fairly conclusive therefore that the acids of steps II and III have analogous structures but differ in their readiness to add an extra O^{2-} ion.

The reaction of two metavanadate ions and one oxide ion to yield a pyrovanadate ion could be visualized as due to the simultaneous polarization of two V=O bonds of the two ions under the influence of the O^{2-} ion. This results in an induced positive charge on the vanadium cores to which the oxide ion adds to form an oxygen bridge. Charge distribution would yield the pyrovanadate ion:

$$\text{(structural formula)} \qquad (11)$$
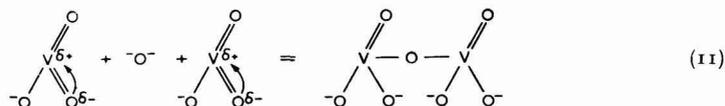
The transformation of metavanadate into pyrovanadate can be effected through molten nitrate[3]. It is reasonable to assume that the reaction follows the same mechanism presented above. The nitrate ion carries, however, a single negative charge and can thus react with one metavanadate ion at a time, according to

$$\text{(structural formula)} \qquad (12)$$

followed by

$$2[VO_3\text{–}O\text{–}NO_2]^{2-} = V_2O_7^{4-} + N_2O_5 \qquad (13)$$
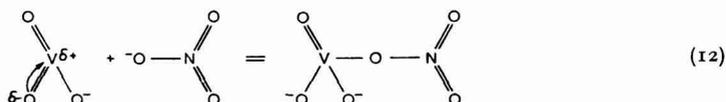
It appears that under certain conditions reaction (13) is hindered and that a good part of the nitrate complex formed, remains in the melt as such (cf. Table 1, column 5). The nitrate complex can be regarded as the monomer of the pyrovanadate ion, so that during its transformation into orthovanadate according to

$$2[VO_3\text{–}O\text{–}NO_2]^{2-} + O^{2-} = 2\ VO_4^{3-} + N_2O_5 \qquad (14)$$
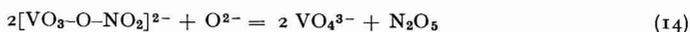
it consumes the same quantity of O^{2-}. This explains the experimental observation that steps II and III together require the same amount of Na_2O_2 calculated for reaction (10).

We must admit at this stage, however, that the conditions leading to stabilization of the nitrate complex are not known to us. Thus, although it has been established that this complex results from the interaction of metavanadate with molten nitrate and that when metavanadate is added to pure nitrate, all the complex formed changes to pyrovanadate (Fig. 4), on the other hand, in the presence of both pyrovanadate and the nitrate complex, about 50% of the added metavanadate is found in the form of the complex.

In contrast to pyrovanadate generated *in situ* by the action of $NaVO_3$ on molten KNO_3, a commercial sample of pyrovanadate reacts very slowly with sodium peroxide. Equilibrium potentials can be measured only after relatively long periods. A titration curve of 10 points required about 12 h to be traced properly. As a result of the difference in reactivity, the quick neutralization of $NaVO_3$–$Na_4V_2O_7$–KNO_3 melts gave an end point which corresponded only to the pyrovanadate resulting from metavanadate, *i.e.*, the mixture behaved as if it contained no original pyrovanadate. If, however, the mixture was left for a few hours after the first end point had been reached, the potential of the oxygen electrode levelled up again and the rest of pyrovanadate was easily determined.
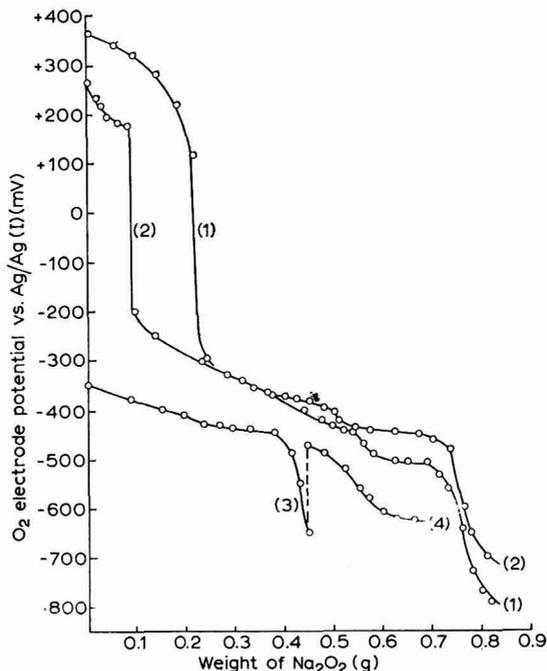
Fig. 5. Potentiometric titration curves of mixtures of V_2O_5 + $Na_4V_2O_7$ at 350°. (1), 1.000 g V_2O_5 + 0.500 g $Na_4V_2O_7$; (2), 1.000 g V_2O_5 + 1.000 g $Na_4V_2O_7$; (3), 1.000 g V_2O_5 + 0.430 g Na_2O_2 + 1.000 g $Na_4V_2O_7$, quick neutralization; (4), as (3), slow neutralization.

The addition of $Na_4V_2O_7$ to V_2O_5–KNO_3 melts gives rise to results which are of interest. Curves 1 and 2 of Fig. 5 are titration curves for V_2O_5–KNO_3 melts to which different quantities of pyrovanadate were added. The three neutralization steps characteristic for V_2O_5 were easily recorded. The tracing of step II offered no diffi-

culty. The quantities of Na_2O_2 consumed along each of the three steps are given in Table id. It can be seen from the figures in this table that the consumption of sodium peroxide during step I is less than that for V_2O_5 alone, while step III requires more Na_2O_2. These observations can be easily explained by taking into consideration the fact that $Na_4V_2O_7$ is basic with respect to V_2O_5. Metavanadate will thus form according to

$$V_2O_5 + V_2O_7{}^{4-} = 4\ VO_3{}^- \tag{15}$$

and will react with nitrate to yield pyrovanadate and the nitrate complex in quantities proportional to the added pyro-salt. Except for the decrease in the quantity of Na_2O_2 consumed along step I, the addition of pyrovanadate to V_2O_5–KNO_3 melts produces the same effect as $NaVO_3$.

It is of interest to observe that when the first neutralization step of V_2O_5 is eliminated by the addition of Na_2O_2 before the introduction of pyrovanadate into the melt, the quick neutralization records only the pyrovanadate resulting from V_2O_5 (Fig. 5, curve 3). The melt behaves as if it is free from any added pyrovanadate. If, however, enough time is allowed to elapse after the attainment of this equivalent point, the potential of the oxygen electrode rises again and the extra pyrovanadate can be quantitatively determined (Fig. 5, curve 4). Apparently this behaviour is related to a difference in the reactivity of the two forms of pyrovanadate.

These results clearly demonstrate that metavanadate cannot be prepared by fusing V_2O_5 with KNO_3 as claimed by NORBLAD. The metavanadate formed is a strong Lux-acid which quickly reacts with the nitrate base-electrolyte to produce pyrovanadate and a nitrate complex of the probable formula $[VO_3–O–NO_2]^{2-}$.

SUMMARY

The reaction between V_2O_5 and molten KNO_3 is studied potentiometrically by conducting acid–base titration experiments *in situ*. An oxygen electrode is used as indicator electrode. The titration curves show three distinct potential drops. The first step is due to the transformation of V_2O_5 into metavanadate which reacts instantly with the nitrate base-electrolyte to yield pyrovanadate and a nitrate complex of the probable formula $[VO_3–O–NO_2]^{2-}$. Both compounds change upon neutralization into orthovanadate along the second and third steps, respectively, of the titration curves.

The effect of varying the temperature, fusion time, concentration of V_2O_5 and the effect of the addition of increasing quantities of $NaVO_3$ and $Na_4V_2O_7$ on the titration curves of V_2O_5–KNO_3 melts is investigated in detail. A mechanism accounting for the disappearance of the pentoxide is proposed. The reaction between V_2O_5 and molten KNO_3 is zero-order with respect to V_2O_5.

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REVIEW

POLAROGRAPHY IN MOLTEN SALTS

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INTRODUCTION

For over half a century fused salts have been used as electrolytic baths in the production of aluminium and magnesium metals. More recently, the possibility of obtaining other metals such as beryllium, titanium, zirconium, molybdenum, thorium and even uranium by fused salt electrolysis has been recognised[1]. Molten salt solvents are also playing an increasingly important part in several branches of nuclear technology[2,3] and as baths for heat treatment of metals. Because of these developments, electrochemical behaviour in them has been extensively studied. The present article reviews the recent progress in the application of the polarographic method to the study of molten salt solutions. Since improvements in methods of solvent preparation, fabrication of the indicator electrodes, development of depolarized reference systems, etc., have considerably improved the reproducibility of results, the scope of the present review has been extended to include also the progress made in these fields.

METHODOLOGY

Solvent preparation

In comparison with aqueous solutions, large quantities of salts have to be used in the preparation of a fused-salt solvent and therefore the level of heavy-metal impurities could be high even when chemically pure grade substances are used. In addition, if the salts are not completely dehydrated before fusion, impurities may arise as a result of hydrolytic decomposition of the solvent, and thus considerable attention has to be given to the preparation of a molten salt solvent. In most of the investigations reported up to about 1950, this aspect was not given due consideration; this resulted in some confusion in the literature concerning the reproducibility of polarographic data in molten salt solutions. The method employed for the preparation depends upon the solvent chosen, but it may involve several steps such as (i) predrying of the salts by prolonged evacuation at room and/or elevated temperatures[4-7] and (ii) fusion in inert[8] or other gaseous[2,6,7,9,10] atmospheres to avoid hydrolytic decomposition by traces of moisture still held by the salts, followed by elimination of any gas dissolved in the melt. A final scavenging step may involve treatment with a metal which has a high reducing potential in the solvent used[11] or pre-electrolysis using inert electrodes[5], filtration, etc. The electrolytic cell in which the solvent is to be prepared must be suitably designed so that the various operations may be carried

out without exposing the melt to the atmosphere. A slow stream of an inert gas (argon or nitrogen) is usually provided over the melt surface during experiments. The purity of a melt may be judged by a small polarographic residual current[5,7] and a wide decomposition potential span, limited by the electrolysis of the solvent itself.

Techniques of addition of the solute to the melt, under an inert atmosphere, have been developed[5]. In many cases the external addition can be obviated by coulometric, *in situ*, generation of the metal ions by anodic dissolution of metal foil or rod using a constant current source. In this case it is necessary to ensure that the dissolution occurs with a 100% current efficiency[12].

Indicator electrodes

A dropping mercury electrode (D.M.E.) has been used as an indicator electrode for the polarographic investigations in low-melting binary[13] and ternary[14,15] molten alkali nitrates and chlorides[16], ammonium formate[17], urea[18], etc., up to about 180°. At higher temperatures (400°–500°), dropping bismuth[19] and dropping lead[20] electrodes have been used. A dropping electrode provides a continually renewed surface of reproducible area and a homogeneous diffusion field so that the mass transport at the electrode is amenable to rigorous mathematical treatment. However, its use would have to be restricted to the study of the deposition of ions of metals less noble than that of the electrode. Further, molten metals are partly dissolved in molten salt systems and also react with them, as for example[19]:

$$2 \text{ Bi (dropping electrode)} + 3 \text{ PbCl}_2 \text{ (in solvent)} = 2 \text{ BiCl}_3 \text{ (in solvent)} + 3 \text{ Pb (Bi)}$$
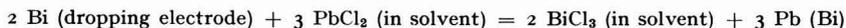
It is also quite difficult to realize a dropping metal electrode with a strictly definite and constant dropping rate. Most workers have therefore preferred to use a solid micro-electrode as the indicator electrode for polarographic and other electrochemical investigations in molten salts. An ideal micro-electrode should be very noble and provide conducting surface of known area and geometry, besides being rugged and durable. It may be prepared by sealing a suitable length of a noble-metal wire of *ca.* 0.1–0.3 mm diam. into an insulating material, the coefficient of expansion of which matches with that of the metal. The wire-end should protrude out of the seal (cylindrical electrode) or be fused to form a bead (spherical electrode) or ground flush with the seal so as to expose only the cross section of the wire (planar electrode). Platinum- and tungsten-metal wires sealed into glass have commonly been employed. The sealing may be done directly by using special types of glass or through graded seals[21]. The maximum working temperature would be about 20–50° lower than the softening point of the glass used. Platinum sealed into soda-lead glass (Corning 0120) has been used up to 475°[22]. Similarly, thin platinum and tungsten wires sealed into pyrex and other borosilicate glasses have been employed upto 600°[23]. For still higher temperatures tungsten was sealed into Vycor with graded seals[12] and used at 740°. It is difficult to get a good metal-insulating material seal for use at temperatures of the order of 1000° so that polarographic micro-electrodes of defined area and geometry for use under these conditions cannot be satisfactorily fabricated.

A solid micro-electrode may have a rough surface and may be covered with an oxide-layer formed during its fabrication or exposure to the atmosphere. The electrode can be polished to a mirror-surface with fine emery or metallurgical alumina and should be given a suitable pre-treatment before use.

Although it is difficult to define the *true* area of a solid micro-electrode, for linear diffusion conditions one is concerned with the *apparent* or *projected* area of the micro-electrode. In numerous studies (see under the heading — Applications) proportionality of electrolysis current with the apparent or projected area of the micro-electrode has been shown.

With a stationary solid micro-electrode and slow rates of polarization as in d.c. polarography, the convective transfer of reducible ion is increasingly difficult to eliminate as the temperature is raised; this may be avoided by employing short polarization time as in oscillographic polarography. Alternatively, one may employ forced convection condition by agitating the solution, *e.g.*, by using a rotating micro-electrode or a rotating disc-electrode. LYALIKOV AND KARMAZIN[24,25] on the other hand, developed a gas-flushed indicator electrode in which a platinum needle was surrounded by an open-end glass tube immersed into the solution; an inert gas, led through the tube, bubbled into the melt. The needle came into intermittent contact with the solution each time a gas bubble escaped and the solution was kept stirred. The polarograms obtained with such an electrode were similar to those obtained with a D.M.E. and could be recorded automatically. With the improvements suggested by FLENGAS[26] and HILLS, INMAN AND OXLEY[27,28] the height of undamped diffusion-current wave was independent of the bubbling rate and depth of immersion of the electrode in the melt, etc., and was a linear function of the depolarizer concentration. This electrode has considerably enhanced the scope of applicability of polarography as an electroanalytical tool in molten salts at temperatures higher than had been previously possible. The rate of polarization does not appear to have any influence[9] on the shape or height of the polarographic wave for stationary micro-electrode although for a rotating micro-electrode the wave height increased significantly with increase in rate of polarization[29].

Reference electrodes

A calomel half-cell is almost universally employed as the reference for polarographic studies in *aqueous* medium. There is as yet no such reference system for fused salt solutions because of the dependence of the electrode potential on the nature of the solvent.

Several workers have used, as reference, platinum[23,26,29–35], silver[36,37], aluminium[38], lead[39] and bismuth[19] pools and even graphite[40] dipping into the melt*. Much polarographic data regarding decomposition potentials, half-wave potentials, etc. *vs.* these metals as reference electrodes have been presented, the potential of each electrode having been considered constant and arbitrarily given a zero value. In the absence of a known potential determining equilibrium the function of such a system as reference has not been unambiguously interpreted. It possibly arises from the anodic generation of a small concentration of metal ions in the vicinity of the electrode surface, but it has also been suggested (at least in halide melts) that platinum, for example, functions as an oxygen electrode[41] due to traces of moisture which could be held in the melt even at relatively high temperatures[42,43]. To some extent, such an electrode may be reversible, stable and reproducible, but it can be regarded as non-polarizable only to a first approximation. Recent work by DELIMARSKIĬ[44]

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* Only representative references are included here.

has shown that it may be polarized to the extent of several millivolts in the course of obtaining a polarogram. The data obtained with such a reference, are therefore useful only on a relative basis. A larger concentration of the metal ion in the melt in contact with the metal foil (or rod) gives to it the desired depolarizability. Systems Ag/Ag(I)[45] and Pt/Pt(II)[12,22,46-48], have been used as references for polarographic work and were found to be reversible, reproducible and stable with time. Platinum metal is not easily oxidized and although silver forms several oxides at moderate temperatures, these volatilize on heating to about 300° so that the electrode surface is always clean[49]. Other metal–metal ion couples used as polarographic references are Pb/Pb(II)[50] and Bi/Bi(III)[51]. Ag/AgCl (solid)[13] and Ag/AgBr(solid)[44] have been used as reference electrodes of the second kind, in molten nitrates. In the ternary eutectic LiNO₃–NaNO₃–KNO₃, STEINBERG AND NACHTRIEB[15] even used a calomel as reference but this obviously cannot be used at temperatures higher than about 200°.

<div style="text-align:center">THEORY OF POLAROGRAPHY IN MOLTEN SALTS</div>

Theoretical relationships for the concentration dependence of diffusion current and for the current–voltage functions of polarographic waves involving reversible and irreversible processes, with and without kinetic control, in stirred and unstirred solutions have been developed[52,53]. Most electrode processes in molten salts are polarographically reversible and without kinetic complications and the following equations would cover the different cases so far studied*. The solvent also serves as the supporting electrolyte.

1. Unstirred solutions

(a) *Dropping metal electrodes.* The limiting current (i_1) is given by the Ilkovič equation[54]:

$$i_1 = 3455 \, nD^{\frac{1}{2}}C \, (md)^{\frac{2}{3}}t^{\frac{1}{6}} \tag{1}$$

where, i_1 (μA) is measured as the maximum current of the drop; t is the drop-time in sec; m is the mass (mg) of the dropping metal of density, d, flowing per sec; D is the diffusion coefficient and C the concentration (mmoles/l) of electroactive species. For more accurate work the modified form of the above equation[55] may be used. This forms the basis of polarography as an electroanalytical tool. The diffusion current constant, $i_1/Cm^{\frac{2}{3}}t^{\frac{1}{6}}$, being independent of the capillary characteristics, enables evaluation of the diffusion coefficient.

The current–voltage characteristics of polarographic waves, in the case where the deposited metal forms an amalgam or an alloy with the dropping metal, is expressed by the Heyrovský–Ilkovič equation[56]:

$$E_{\text{d.e.}} = E_{\frac{1}{2}} - \frac{2.303 \, RT}{nF} \log \left(\frac{i}{i_d - i} \right) \tag{2}$$

On the other hand, if the deposited metal is insoluble in the dropping metal or does not form an alloy or the extent of alloy formation is insignificant during the time of observation, so that the activity of the deposited metal may be regarded as constant,

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* For detailed considerations see refs. 52,53.

the current–voltage functions of the polarographic wave would be expressed by the equation[53]:

$$E_{m.e.} = E_m^0 - \frac{2.303\,RT}{nF} \log \frac{k_s}{f_s} + \frac{2.303\,RT}{nF} \log (i_d - i) \tag{3}$$

where E_m^0 is the standard potential of metal whose ions are being reduced at the electrode, f_s is the activity coefficient of metal ion in the solution and k_s the proportionality constant; other symbols in eqns. (2) and (3) have the usual significance.

The half-wave potential would be independent of solute concentration in the first case but would shift in a positive direction with increase in the depolarizer concentration in the second.

(b) *Solid microelectrodes.* The limiting current for a linear diffusion electrode (planar) has been given[51] as

$$i_1 = \frac{nFADC}{\delta} \tag{4}$$

where, δ is the effective thickness of the diffusion layer and A, the area of the microelectrode. For a cylindrical electrode, concentration, C, has to be raised to a power of about $1 \cdot 2$ [57].

The deposition of the metal ions at a stationary *solid* micro-electrode has been regarded as analogous to the deposition of a metal insoluble in mercury at a D.M.E., so that the current–voltage characteristics would be similarly expressed by eqn. (3). This has been confirmed by several workers[12,29,47,48,58] and the slopes of the $E_{m.e.}$ vs. log $(i_d - i)$ plots, and the variation of half-wave potential with concentration have been found to be in reasonable accord with the calculated values, slight variations being ascribed to the existence of non-ideal diffusion situations and/or inconstancy of the diffusion-layer thickness[47,51].

On the other hand in a large number of publications[20,32,34,36,37,48,59-65] attempts have been made to describe the polarographic wave even on a *solid* micro-electrode by a Heyrovský–Ilkovič type of equation. The present author found that such a situation did arise, e.g., in the polarography of cadmium(II) and lead(II) in molten magnesium chloride–sodium chloride–potassium chloride eutectic[48] using a platinum micro-electrode as the indicator electrode. Equation (2) represented the current–voltage characteristics of the polarographic wave, the $E_{m.e.}$ vs. log $[i/(i_d - i)]$ slopes were rectilinear, their slopes agreeing with the calculated values and $E_{\frac{1}{2}}$ was, within limits of experimental error, independent of metal ion concentration. On the other hand, $E_{m.e.}$ vs. log $(i_d - i)$ plots in these cases were curved. At the working temperature (475°) both metals were deposited as liquid on the micro-electrode and since in this state they are known to attack platinum even at relatively lower temperatures[66], the variable activity of the metal deposited on the platinum micro-electrode could be ascribed to *surface-alloy* formation. It would be difficult to visualise this (*surface-alloy* formation) when a metal is deposited as *solid* on platinum (or tungsten) micro-electrodes. Even if it did occur, it would be rather slow and perhaps of no consequence, if for the duration of the observation (2–3 min) the equilibrium metal activity at the micro-electrode did not change significantly. However, concentration depolarization leading to the applicability of the Heyrovský–Ilkovič equation for the polarographic waves obtained with a solid micro-electrode could also arise because of other factors such as: chemical interaction between the products of electrolysis and the molten

electrolyte; the solution of the products into the melt; the diffusion of the products into the electrode[65], etc. Unless independent observations support the change in metal activity at the electrode surface, it would perhaps be incorrect to try to explain the $i-E$ characteristics of a polarographic wave obtained on a solid micro-electrode using the Heyrovský–Ilkovič equation. This may as well be the reason for the apparent existence of unusual oxidation states[20,34,67-70]. Of course, the Heyrovský–Ilkovič equation would always be applicable in the case of reduction and oxidation of metal ions from one oxidation state to another even at a solid micro-electrode.

Recently, DELIMARSKIĬ et al.[60] have shown that eqns. (2) and (3) should in fact be regarded as special cases of a more generalized equation which for a reversible electrode process has the form

$$E = \text{constant} - \frac{RT}{nF} \ln \frac{a_m'' - \left(\frac{i_m'' - i''}{x''}\right)}{\frac{i_d - i}{x'}} \qquad (5)$$

where, x' and x'' are constants for the speed of concentration polarization and concentration depolarization respectively, i'' the speed of depolarization, i_m'' the maximum speed of depolarization and a_m'' the activity of pure separating metal. This reduces to eqn. (2) for $i_d \leqslant i_{dm}''$ and to eqn. (3) for $i_m'' = i''$.

Consequently, the applicability of eqns. (2) or (3) for a reversible process is thus completely defined by the ratio i_d/i_m'', so that under a different set of conditions the same electrode process could also be described by eqns. (2) and (3). Examples have been given of the interpretation of actual polarograms for the reversible discharge of metals from melts[71].

2. Stirred solutions

It has been pointed out[52] that the Nernst concept of the diffusion layer for the transport of depolarizer to the micro-electrode in a stirred solution is inadequate. Several workers have applied principles of hydrodynamics to the mass transfer processes[72]. However, in view of the complexities, complete solutions have been obtained under relatively restricted conditions.

Rotating disc electrode. For the conditions where a flat disc of very large area (A) rotates with a constant angular velocity (ω) about an axis perpendicular to the plane of the disc, in an infinite volume of the solution, containing an excess of the supporting electrolyte, and assuming a laminar flow of the solution, the limiting current(i_l) is given by the relation[72]

$$i_l = 0.62 \; nFAD^{\frac{2}{3}}\omega^{\frac{1}{2}}Cv^{-\frac{1}{6}} \qquad (6)$$

where v is the kinematic viscosity of the solution (cm^2/sec).

3. Oscilloscopic polarography

Single-sweep method has been generally used. The $i-E$ relationships for the waves have been described[52], the peak current (i_p) for a reversible process being given by

$$i_p = \frac{Bn^{\frac{3}{2}} F^{\frac{3}{2}}}{R^{\frac{1}{2}}T^{\frac{1}{2}}} \cdot ACD^{\frac{1}{2}}v^{\frac{1}{2}} \qquad (7)$$

where v, is the voltage-sweep rate, the numerical factor B having a value 0.452 for the case where the activity of metal deposited on the micro-electrode may be regarded as variable due to amalgam or *surface-alloy* formation or dissolution into the solvent. In the other case, where the electrode process leads to an insoluble product the value of B is 0.611. In the former case the peak potential is independent of depolarizer concentration, but in the latter it shifts in the positive direction with increase in concentration.

APPLICATIONS

Early polarographic studies in molten salts were carried out in low-melting binary- and ternary-nitrates so that techniques of aqueous work could be applied directly or with little modification. NACHTRIEB AND STEINBERG[14,15] studied the reduction of Ni(II) in fused $LiNO_3$–NH_4NO_3–NH_4Cl at 125° and of Pb(II), Zn(II), Ni(II) Co(II), Cd(II) in fused $LiNO_3$–$NaNO_3$–KNO_3 at 160°, using a dropping mercury electrode as the polarizable cathode. The current–voltage characteristics obeyed the Heyrovský–Ilkovič equation. The diffusion coefficients and activation energy for diffusion process, etc., were calculated. Polarographic behaviour of Pb(II), Cd(II) and Zn(II) in the fused salt, $LiCl$–KCl–$AlCl_3$ (m.p. 120°), at 160° using a D.M.E. as the indicator electrode is also reported[16]. The electrode reactions were reversible and plots of $E_{d.e.}$ *vs.* $\log[i/(i_d - i)]$ were straight lines with the slopes agreeing with theoretical value for the 2-electron discharge process. Above 200° the vapour pressure of mercury becomes rather high and a D.M.E. cannot be conveniently used as an indicator electrode. A platinum micro-electrode was used for studying the polarographic behaviour of several metal chlorides and metal nitrates in molten KNO_3[25,61,73], $NaNO_3$[31,74] and $NaNO_3$–KNO_3[32,35,58]. In some cases the wave obeyed a Heyrovský–Ilkovič type equation, its applicability being ascribed to the formation of *surface-alloys* on the platinum electrode[61]. LYALIKOV[25] used a gas-flushed platinum micro-electrode. Under better controlled conditions, FLENGAS[26] used this electrode in the polarographic reduction of Ag(I) in molten $NaNO_3$–KNO_3 in the temperature range 242–322°; the solubility products of AgCl and AgBr in this melt, determined by amperometric titration method, were in good agreement with those obtained by other methods[75].

In most of the polarographic investigations in molten nitrate referred to above, the residual current was found to be markedly temperature-dependent and it sharply increased at -0.8 to -1.5 V (*vs.* platinum-foil anode) depending upon the system studied. The narrow decomposition potential span in these solvents as compared to halides (2.8–3.0 V) is incomprehensible on theoretical grounds. This aspect was considered in detail by HILLS AND JOHNSON[35]. It was shown that the steeply-rising current, earlier attributed to the deposition of alkali metals is, in fact, a sharp maximum connected principally with the surface state of the electrode.

The work in molten nitrates is confined to temperatures of the order of 300–350°. At higher temperatures, the melt itself undergoes thermal decomposition. Alkali and alkaline earth metal halide melts although needing higher working temperatures (about 450–600°) are thermally stable over a wider temperature range and have been used up to about 800°. These melts, prepared under controlled conditions, also provide a wide decomposition potential span ~ 2.5 V, limited by the electrolysis of the solvent itself and hence have been extensively used as solvents for polarographic studies. BLACK AND DE VRIES[29] studied the polarography of several ions in a fused

KCl–LiCl eutectic between 380° and 450° with a solid platinum micro-electrode and also a rotating micro-electrode as cathode, and a platinum foil as anode. LAITINEN *et al.*[47] used an improved method of preparation of the solvent. With Pt/Pt(II) in the melt as reference, they studied the polarographic characteristics of cadmium, bismuth, chromium, copper, zinc, thallium, indium, lead, tin, gallium and aluminium chlorides in this solvent. In general, high-melting metals gave dendritic deposits which caused an increase in the micro-electrode area and hence an increase in electrolysis current with time.

HEUS AND EGAN[19] using a dropping bismuth as indicator electrode and a bismuth metal pool anode, studied the behaviour of lead, zinc and cadmium chlorides in the above solvent (LiCl–KCl eutectic) at 450°. By using the Ilkovič equation the diffusion coefficients for Pb(II) and Cd(II) were found to be 1.7×10^{-5} and 1.8×10^{-5} cm^2 sec^{-1} respectively, which agree fairly well with those obtained by LAITINEN *et al.*[76,78] and GAUR[77] by chronopotentiometric measurements. If the solute concentration was 7–8 mmoles/l, polarographic maxima did not interfere with the measurements. NARYSHKIN *et al.*[20,39] studied the polarographic behaviour of several metal chlorides dissolved in LiCl–KCl eutectic using a stationary tungsten micro-electrode and also a dropping lead electrode. In both cases the $E_{m.e.}$ *vs.* log $[i/(i_d - i)]$ plots were rectilinear. However, the valence changes in these studies for Zn(II), Al(III), Mn(II) and Be(III) which were 1.8, 1.98, 1.15 and 2.12 respectively, did not correspond with the expected values.

The ternary eutectic, magnesium chloride–sodium chloride–potassium chloride (50 : 30 : 20 moles per cent) with m.p. 396°, has been reported[79] to be a useful solvent for extraction of fission products in liquid metal fuel reactors. GAUR AND BEHL[22,48] studied the polarographic behaviour of several chlorides in this solvent at 475° using a platinum micro-electrode as cathode and Pt/Pt(II) in the melt as reference. Limiting waves were obtained only in the reduction of those ions (Cd^{2+}, Pb^{2+}, Sn^{2+}) where the metal was deposited as *liquid* on the micro-electrode at the working temperature (475°); in these cases the limiting current was proportional to metal ion concentration in the solution. In other cases where the metal was deposited as *solid* on the micro-electrode the electrolysis current at the end of the S-shaped curve increased with increasing cathodic polarization and with time; this severely limited the analytical utility of these polarograms. It was found that the current–voltage characteristics of the polarographic wave in the former case (metal deposited as liquid) were expressed by the Heyrovský-Ilkovič equation and this was ascribed to *surface-alloy* formation.

Equimolar NaCl–KCl, m.p. 660°, has been used as solvent for polarographic studies in the temperature range 700–740°. DELIMARSKIĬ AND KUZ'MOVICH[34] studied the polarographic behaviour of Cu(I), Cu(II), Ag(I), Zn(II), Cd(II), Tl(I), Co(II) and Ni(II) chlorides using a platinum micro-electrode; in some cases the current–voltage characteristics of the polarographic waves were expressed by eqn. (3) but in others the Heyrovský–Ilkovič equation was better obeyed. Energies of activation for the diffusion current were in the range 3–6 kcal/mole. Manganese chloride showed[70] several unusual oxidation states and iron chlorides gave[80] waves corresponding to Fe(III)–Fe, and Fe(II)–Fe. NARYSHKIN AND MOGILEV[38] used a tungsten cathode. In these studies the details for the fabrication of micro-electrodes and information as to whether these provided conducting surface of definite area, were not available to the present reviewers. MARICLE AND HUME[12] used tungsten-in-Vycor micro-

electrodes with areas of 7.4 and 1.2 mm² and platinum/platinum(II) in the melt as reference. The limiting current in the reduction of Ag(I), Ni(II), Fe(II), Cu(I) chlorides in KCl–NaCl at 740° were proportional to their concentration with a standard deviation of 5–8%. The effects of electrode area, rate of potential scan and temperature on the limiting current were also investigated. The *increasing current tendency* earlier observed by LAITINEN *et al.*[47] for the deposition of solid metals on micro-electrodes was not found to be serious with electrodes of larger areas. However, in the latter case rather dilute solutions have to be employed to prevent the reference system from being polarized.

REMPEL[40] studied the polarographic waves in molten carnallite using a molybdenum cathode and graphite as anode at 735°. The observed wave height was proportional to water retained in the melt and was ascribed to the hydronium ion. The current–potential characteristics of this wave were expressed by the Heyrovský–Ilkovič equation if the electrode potential ($E_{m.e.}$) was corrected for the hydrogen overvoltage, (η), on molybdenum in carnallite, given by the Tafel equation. Plots of $E_{ccrr.}$ (= $E_{m.e.} - \eta$) vs. log $[i/(i_d - i)]$ gave a slope of 0.207 in good agreement with the calculated value of 0.200 for a one-electron change at 735°. It was thus concluded that hydrogen of the water dissolved in molten carnallite was present as H^+.

At still higher temperatures, difficulties in fabricating micro-electrodes with defined area and geometry are considerably increased and so is the problem of elimination of convection. None-the-less, polarographic studies in molten salt solvents under these conditions are important from a practical point of view. For analytical work one could use a noble-metal wire dipping into the melt as the micro-cathode or a gas-flushed micro-electrode. PANCHENKO[64] reported the behaviour of Ag(I), Pb(II), Cd(II) chlorides in molten KCl at 800° using a platinum electrode. The limiting current was proportional to the concentration of the dissolved salt and the polarographic wave obeyed the Heyrovský–Ilkovič equation. DELIMARSKIĬ AND KALABALINA[67,68] used molten borax as solvent for solutions of various metal oxides at 820°. In each case the limiting current increased linearly with concentration so that the polarograms could be used for the quantitative determination of these oxides in the solution. The activation energies for the diffusion processes were of the order of 20–30 kcal/mole indicating the presence of complex and relatively slow-moving ions in this melt. The analysis of the polarographic waves was not satisfactory however, *e.g.*, the prelogarithmic term for the reduction of copper oxide corresponded to a value between a 1- and 2-electron process, that for cadmium oxide between a 2- and 3-electron process and for iron and cobalt oxide for single electron processes. Polarographic behaviour of metal oxides in several other molten solvents such as sodium metaphosphate[81–83], Li_2CO_3–Na_2CO_3[84] and borosilicates[85] in the temperature range 650–1000° using a stationary platinum micro-electrode have also been recently reported.

Polarography of metal–molten salt system

Polarographic technique has also been employed for the study of some metal–molten metal salt systems. EGAN[86] showed that excess lead dissolved in molten lead chloride predominantly in the form Pb_2^{2+}, although to some extent this dissociated[87] into $2Pb^{2+}$. Polarograms of bismuth in molten bismuth chloride using a platinum or tungsten micro-electrode *vs.* Bi–BiCl₃ reference were found[51] to give anodic waves

indicating the oxidation of a soluble sub-halide entity; the anodic limiting current was proportional to the metal concentration up to about 0.2 mole per cent of Bi in molten $BiCl_3$. The studies were, however, inconclusive with respect to the oxidation state and the degree of association of the bismuth species, but this appeared to be Bi^+.

Polarography of complexes in molten salts

The method of DE FORD AND HUME[88] for evaluating the stability constants* of complexes in solution from the shift in the polarogram due to the addition of a ligand was employed by CHRISTIE AND OSTERYOUNG[13] in the study of the chloro-complexes of Pb(II), Cd(II) and Ni(II) in fused $LiNO_3$–KNO_3 at 180° using a D.M.E. as the polarizable electrode. Similar studies for the bromo-complexes of lead and cadmium could not be made because in the presence of bromide ions in the melt, the polarographic waves showed a maximum and accurate determinations of half-wave potentials were not possible.

DELIMARSKIĬ *et al.*[90] have derived equations similar to the above for the polarograms obtained on a solid micro-electrode and involving various types of electrode processes. The stability constants of the chlorocomplexes of Pb(II), Ni(II) and Cd(II) in molten $NaNO_3$–KNO_3 eutectic in the temperature range 240–280° were evaluated[91].

Anodic polarography in molten salts

There is relatively smaller potential span for the study of anode processes in molten salts. This is frequently limited by the depolarizing action of the dissolution of the metal used as indicator electrode or the oxidation of the anion. CHOVNYK[45] obtained a polarogram for the anodic process Sn(II)–Sn(IV) in molten equimolar $AlBr_3$–NaBr at 226° on a platinum micro-electrode; the polarograms obeyed the Heyrovský–Ilkovič equation. Such a process was not observed in molten chlorides[48]. REMPEL AND MALKOVA[50] studied the oxidation of sulphide ion in molten KCl–NaCl on a graphite rod coated with a refractory glass as the indicator electrode, the height of the limiting wave being proportional to sulphide ion concentration in the solution. LYALIKOV AND NOVIK[32,92] reported the behaviour of bromide, iodide and nitrite ion in molten nitrates. GAUR AND BEHL[48] studied the anodic process Cr(II)–Cr(III) on a platinum micro-electrode in $MgCl_2$–NaCl–KCl; anodic waves for Fe(II)–Fe(III) and Cu(I)–Cu(II) could not be obtained as they overlapped with that of platinum dissolution.

Derivative polarography, oscillographic polarography and polarography with a rotating disc electrode

In the analysis of molten salt solutions containing several reducible (or oxidisable) ions the difficulties in their resolution are similar to those encountered in aqueous work. For overlapping waves, one could employ a.c. polarography or obtain derivative polarograms using a differentiating unit. In molten, equimolar $AlBr_3$–NaCl, CHOVNYK[93] obtained derivative waves for successive discharge of Cu(I) and Co(II) as also for Co(II), Pb(II) and Cd(II); ordinary polarograms for these gave overlapping waves. The peak heights were proportional to the depolarizer concentration. PANCHENKO[94] used a rotating solid electrode for the derivative polarograms of Ag(I), Pb(II) and Cd(II) chlorides in KCl–LiCl eutectic.

The cathode ray oscillograph has recently been used for polarographic studies in

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* For a critical evaluation, see refs. 89, 89a.

molten salts. This offers several advantages over the d.c. polarographic method. By employing a fast sweep rate, the diffusion-layer thickness can be made so small that the electrolysis current is insensitive to natural or even forced convections. Another advantage is the linearity of the capacity current over the whole of the potential range which can be easily compensated, so that this method is better suited for study of dilute solutions than d.c. polarography. The behaviour of Ag(I) in KCl–LiCl at 500° has been studied by HILLS et al.[23]. The peak current was proportional to Ag(I) concentration in the solution over the concentration range 5–30 mmoles/l. DELIMARSKIĬ AND SHAPOVAL[95] used a multi-sweep method for the study of cathodic and anodic processes in solutions of $CdCl_2$ in molten KCl–NaCl at 720°; the reduction was reversible. Oscillographic a.c. polarography has also been applied to the reversible reduction of various metal chlorides dissolved in KCl–LiCl on a solid platinum micro-electrode[96].

A rotating disc electrode (R.D.E.) can be used with great advantage for polarographic studies in molten salts. Some applications have recently been reported but the full potentialities have not been exploited so far. The limiting current with a R.D.E. at an arbitrarily fixed speed of rotation enables determination of the diffusion coefficients of ions; this would be of value in view of the discrepancies in some values obtained by different electrochemical methods[97].

ĊHOVNYK AND VASHCHENKO[98] studied the discharge of Ag^+ in $NaNO_3$–KNO_3 eutectic at a rotating disc electrode. The diffusion current increased in proportion to the square root of the speed of rotation of the disc in accordance with Levich's theory of convective diffusion[72]; the diffusion coefficient was found to be 0.945×10^{-5} $cm^2 \, sec^{-1}$ which was in good agreement with the value obtained by other methods. DELIMARSKIĬ et al.[99] studied the behaviour of silver, cadmium, manganese, thallium, lead and bismuth chloride in molten KCl–LiCl eutectic (at $420 \pm 2°$). At an electrode revolution rate of 500 r.p.m., good waves were obtained. The experimental variation of limiting current with angular velocity of rotation (ω) was given by the relationship

$$i_1 = K \cdot \omega^{0.58} \qquad (8)$$

The slight variations from Levich's theory appear to be due to edge effect or surface roughness[100]. The diffusion coefficients of cadmium, manganese, thallium, lead and bismuth ions were found to be 7.0, 6.0, 5.0, 4.0 and $3.0 \times 10^{-5} \, cm^2 \, sec^{-1}$, respectively.

In conclusion, polarography offers a convenient electroanalytical tool for *in situ* analysis of molten salt solutions, determination of the oxidation states of metals, the mechanism of the electron transfer process at the micro-electrode, the nature of complexes, etc. However, the ultimate objective of the adoption of this technique *viz.*, for direct analysis of metallurgical slags, glasses, study of reactions at very high temperatures, and corrosion by molten salt solvent, etc. is still far from being achieved.

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Short Communication

Basis of possible continuous self activation in an electrochemical energy converter

Previous studies on the anodic oxidation of ethylene[1,2] and similar unsaturated hydrocarbons[3] on platinized Pt showed that the activity of the electrode decreased with time[4] (Fig. 1), and could be increased again by momentarily increasing its
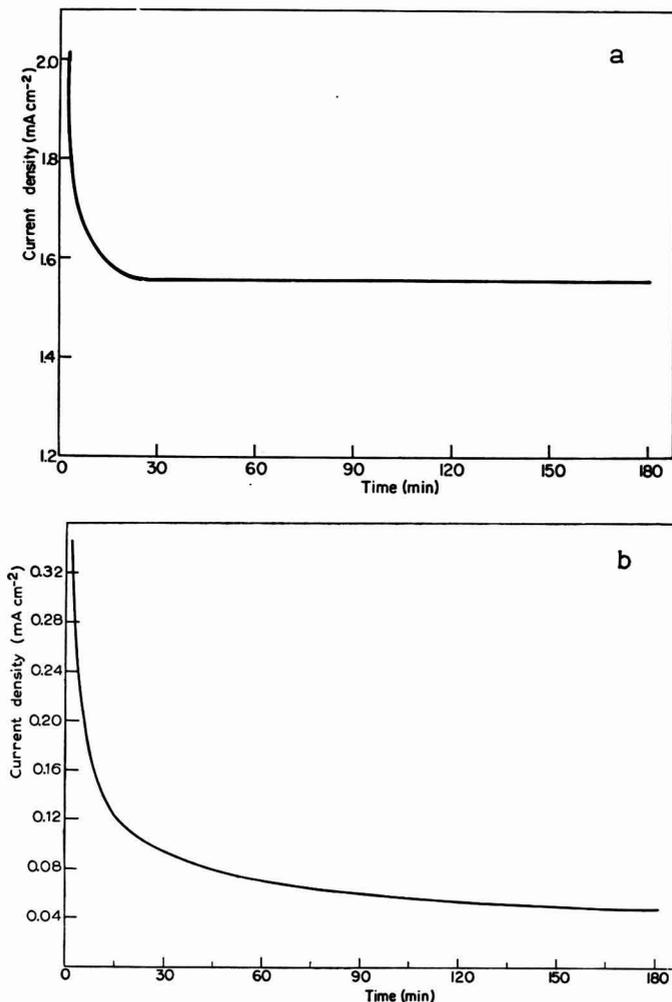
Fig. 1. The deactivation of platinized Pt anodes in the ethylene oxidation reaction: (a), change of current with time at constant potential in acid solution; (b), change of current with time at constant potential in alkaline solution.

potential to a value near to that of oxide formation (about 0.9–1.0 V $vs.$ N.H.E.[5,6]). It may be suggested that a reaction intermediate formed by partial oxidation of the hydrocarbon tends to accumulate on the surface of the electrode and decrease the rate of the reaction, which is proportional to the total number of *free* sites $(I-\theta_T)$ on the surface[2]. When the potential is momentarily increased, this intermediate is rapidly removed from the surface by oxidation to CO_2 and the number of sites available for the first (and, for ethylene, rate-determining) step in the consecutive sequence of reaction steps leading to CO_2 production is thus increased. A similar suggestion was recently made independently by GINER[7] in the study of the anodic oxidation of methanol, where a radical containing carbon and oxygen is supposed to retard oxidation at potentials less positive than 0.6 V $vs.$ N.H.E. for methanol in I N sulfuric acid.
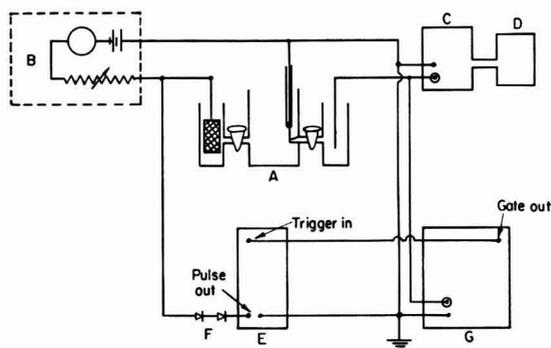
Fig. 2. Block diagram of the electric circuit used: (A), the cell; (B), constant current supply; (C), electrometer; (D), recorder; (E), pulse generator; (F), silicon diodes; (G), oscilloscope.

The use of repeated pulses consuming a small portion of the energy at a hypothetical fuel cell to maintain an electrode catalyst for hydrocarbon oxidation in an activated condition is an interesting possibility and a brief report is given here.

The anodic oxidation of ethylene on small (geometric area, 1 cm²) platinized Pt electrodes in 1 N H_2SO_4 at 80° has been studied. Details of electrode preparation and other experimental details are given elsewhere[1,2]. The electric circuit used in these experiments is shown in Fig. 2. The cell (A) was polarized by a constant current supply (B). Potentials were measured with an electrometer and recorder (C and D). In addition, square pulses produced by the pulse generator (E), were superimposed on the electrode through silicon diodes (F), (to isolate the pulse generator from the circuit during the off time). Transient voltages were measured with an oscilloscope (G), whose output gate was used to trigger the pulse generator.

The experimental procedure involved the introduction of an activated electrode ($cf.$ ref. 2) into the anode compartment and application of a constant current between it and the counter electrode until a steady state was reached. Anodic current pulses of varying width, height, and repetition time from the Tektronix type-161 pulse generator were then superimposed on the constant polarizing current and the variation of potential with time was recorded (Fig. 3). Immediately after the pulse, the

overpotential decreases by 0.15–0.25 V (depending on pulse height) from the initial steady-state value and then begins to increase again.

For the purpose of calculating the per cent gain in power output, let it be assumed that the ethylene anode would be combined in a practical device with an oxygen cathode, giving an overall cell potential of, say, 0.3 V under optimum load conditions (in the present case this would correspond to a (diffusion-limited) current density of 1 mA cm^{-2} on the anode). A unit cell of 1 cm^2 anode area would deliver, without activation, a power of 0.3×10^{-3} W*. The power used to activate it is 0.03×10^{-3} W, i.e., 10% (40 mA at 0.15 V for 0.1 sec every 20 sec) of the hypothetical fuel cell power output and the effect of the activation is to increase the cell potential by about 0.18 V, the corresponding gain in power being 0.18×10^{-3} W, that is 60% total gain in power or 50% net power gain. During the pulse the cell cannot be used as a source
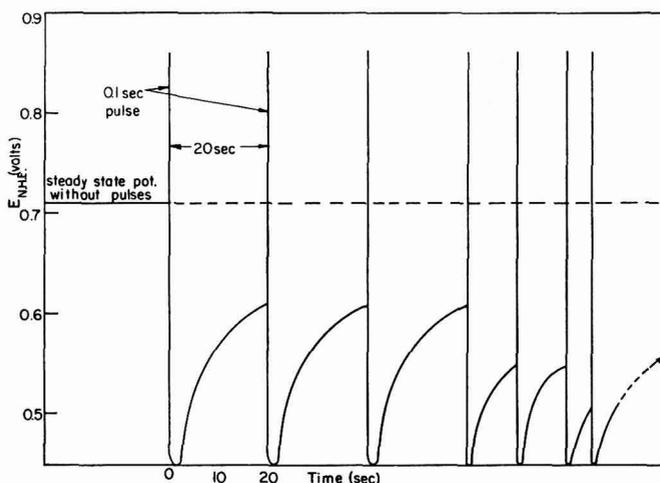
Fig. 3. Extent of activation achieved by pulsing at various intervals. Pulse width, 0.1 sec; pulse height, 40 mA (approx.); steady-state current density, 1 mA cm^{-2}.

of energy, the current passed and the corresponding amount of hydrocarbon burnt are wasted. The current of 40 mA/cm^2 for 0.1 sec in 20 sec corresponds to an average of 0.2 mA/cm^2, out of a total of 1.2 mA/cm^2, thus reducing the current efficiency of the cell from practically 100% to about 83%.

Since the pulse current is in the same direction as the output current, no additional input power would be required in a real electrochemical energy converter to activate the hydrocarbon anode. Thus, e.g., in an oxygen–ethylene cell the anode could be activated by momentarily shorting the terminals of the cell. A transient current would flow corresponding to a transfer of charge from one capacitor to another (the two electrodes acting during a short transient as capacitors) and the change of

potential of each capacitor (electrode) would be inversely proportional to its capacitance, $\Delta V_1 / \Delta V_2 = C_2 / C_1$. The capacitance of the oxygen cathode can be much larger than that of the hydrocarbon anode, and as a result the potential of the former will not change much during the transient and that of the latter could be raised sufficiently to activate the electrode. The resistance of a practical battery will be of the order of $0.1–1$ Ω/cm^2 while the capacitance of the oxygen electrode, assuming that it has a roughness factor of the order of 10^3 and a capacity of $20–500$ μF per cm^2 of real surface area, would be about $0.02–0.5$ F per cm^2 of geometrical area. Thus the time constant involved in reaching the *activation potential* when the cell is shorted, is of the order of $2–500$ msec.

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Book Reviews

Chromatographic Reviews, Volume 5, edited by MICHAEL LEDERER, Elsevier Publishing Company, Amsterdam, London and New York, 1963, ix + 244 pages, 35 illustrations and 51 tables, £3.

The publication of reviews in the *Journal of Chromatography* has ceased consequently, *Chromatographic Reviews* will in the future contain only new material, in contrast to Volume 5 which includes three reviews previously published in the *Journal of Chromatography* in addition to an original monograph and two new reviews.

The book starts with a contribution from WALDMANN-MEYER who discusses in detail, with 259 references, the protein mobilities and ion binding constants evaluated by zone electrophoresis. The main problems appear to have been solved and may well lead to further progress in studies of the electrochemical properties of proteins and other macromolecules.

The next chapter makes envious reading for any routine user of paper and thin-layer chromatography; ARX AND NEHER describe with good illustrations and diagrams the planning that went into the construction of an efficient chromatography laboratory for the Pharmaceutical Research Division of CIBA Ltd.

The ever-interesting relationship between paper chromatographic behaviour and organic structures is discussed on the next 100 pages by GREEN, MARCINKIEWICZ AND McHALE, and interpreted in terms of the electronic theory. This monograph is presented in eight sections, the first describing a new method of tankless, or flat-bed, chromatography for the accurate determination of R_M values. Using this method alkyl dinitrobenzoates are shown to obey Martin's equation with respect to ΔR_M (CH_2). The remaining sections discuss the application of their ideas to a large number of compounds, including phenols, alkoxyphenols, coumaranols, chromanols, tocopherols, vitamins K, ubiquinones, ubichromenols, thienol, *p*-nitrosophenols, and *m*- and *p*-derivatives of benzene. The results are interpretated by consideration of the effect on R_M values of steric and electronic factors, including effects of unsaturation and chain branching, intra-molecular hydrogen bonding, tautomerism and hyperconjugation.

The separation of organic substances by counter-current distribution is surveyed by CASINOVI with 492 references. Then OAKEY reviews the progress made in the application of paper chromatography to the oestrogens, a very important technique in clinical biochemistry and discusses the relationship between mobility and their chemical structures. Useful tables of R_F values of oestrogens in different solvents are given and key references are cited.

The book concludes with a discussion of the application of gas chromatography to inorganic compounds. TADMOR discusses the problems and possible developments of this technique and reviews the separations achieved to date.

The high standard of Elsevier presentation is evident; the layout is excellent, the diagrams clear and the paper of good quality. The book is a mine of information on chromatography and should find a place in every scientific library and laboratory.

LESLIE HOUGH, Chemistry Department, University of Bristol

Atlas d'Equilibres Electrochimiques, by M. POURBAIX, Gauthier-Villars et Cie, Paris, 1963, 644 pages, Fr.140 ($29.00).

The publication of this large collection of data marks the culmination of a programme of work initiated many years ago by Dr. POURBAIX and foreshadowed in his Thesis *Thermodynamique des solutions aqueuses diluées. Représentation graphique du rôle du pH et du potentials*, 1945. This work is probably more familiar in the English translation, by J. N. AGAR, from the second French edition. The reviewer still recommends this translation to anyone making a first acquaintance with the Atlas, since it explains the construction and use of the diagrams more clearly than in the book under review. The object of the book has been to express the probable behaviour of the elements in contact with aqueous solutions at different potentials and pH values, at 25°, with respect to their oxides, hydroxides, ions, oxyions, etc., in a diagramatic form, utilising thermodynamic data. It was considered that such a compilation would be of special value in corrosion and immunity studies and in electro-deposition. Much of the contents has been published elsewhere, mainly in *Electrochimica Acta* and in the technical publications of Cebelcor. Indeed in many cases the information has been transferred directly from the Cebelcor reports to the Atlas, with little change; perhaps some references have been omitted but often there has been, regrettably, little revision of the basic data in branches of electrochemistry where quite considerable subsequent progress has been made. The principal author has had the assistance of a number of experienced and indeed distinguished collaborators to whom due acknowledgement has been made.

The extent of the undertaking is large and in criticising the book one must bear this in mind. The reviewer fears that, unfortunately, some of the derived data may come under the heading of algebraic chemistry, even to the point of demanding a suspension of belief in experimental fact in order to complete the description of the various systems. It would have been most valuable (although the inclusion of the invited contributions from various authors on the applications of the diagrams might then have been uneconomic) if the author, himself, had made a more thorough survey and discussed his reasons for the choice of much of the data in the production of the diagrams, and also the reasons for deciding on which chemical entities to include. Let us for example consider a few of the systems such as those of platinum, nickel and manganese, all of great industrial importance. The anodic surface properties of platinum are complex and but poorly understood, yet the chemical references to the oxides refer to work published in 1907/8, and recent work (*e.g.*, on the preparation of bulk oxides; on the structure of PtO_2; on differences between monolayer- and bulk-oxides; and the existence of cubic Pt_3O_4) is not mentioned. The treatment of nickel is similarly rather out-dated. The use of the abbreviated formulae NiO_2, Ni_2O_3 and Ni_3O_4 conceals the fact that these oxides have not been prepared in an unhydrated form, and the higher oxides, which have been treated as pure crystalline phases, actually show considerable ranges in composition. In addition, it is extremely unlikely that NiO_2 and Ni_2O_3 exist as distinct crystalline phases; if NiO_2 and Ni_2O_3 are distinct phases, why should the positive plate potential Fig. 6, p. 337, fall progressively during discharge?

In the treatment of manganese, a discussion of the probable mechanism of the discharge of the MnO_2 electrode is included, which I am certain is no longer considered

to be the correct mechanism by the senior co-author of this section of the book. A work of this kind which is used as a source of data, should be free from errors which could have been eliminated by a thorough revision of the original reports before final publication.

Some of these matters are, of course, discussed in various places by the author himself and he makes well-considered statements concerning the use of the data, for example in Chapter III, Section 1, p. 55, and Section 4–7, p. 82 and 83. For the non-electrochemist, or perhaps a worker in applied chemistry using the book for the first time, however, and perhaps expecting the contents to be completely authoritative and containing the very best choice of data, there should be, I think, some clear account concerning the limitations, defects and the nature of the difficulties of choice in these matters. These, of course, are only words of warning; the compilation of the data and its display in so lucid a form is definitely of value. Information on all systems is here readily at hand and it is the responsibility of the interested investigator to interpret the diagrams of the systems which are of interest to him.

The book is beautifully printed but the reviewer doubts whether the binding is sufficiently strongly for normal use. The review copy already has a broken spine which suggests that the book, if it were subjected to considerable usage, would need rebinding in quite a short time; this is regrettable in so expensive a book.

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Metodi di Separazione nella Chimica Inorganica, Volumes I and II, edited by M. LEDERER, Consiglio Nazionale delle Richerche, Roma, 1963; Vol. I, 258 pages, $ 12.00; Vol. II, 144 pages, $ 8.00.

These two volumes are the official publications of the lectures presented to a postgraduate Summer School at the Accademia Naz. dei Lincei, in September 1962, by a group of experts in the modern methods used in separating inorganic compounds, under the leadership of Dr. M. LEDERER, who has also edited these books. Those who were present in the beautiful villa La Farnesina to hear these lectures will be pleased to have this record of the course, but the information presented in this form will be invaluable to many other inorganic chemists faced with separation problems. For the English reader, the lectures in Italian may present some difficulty in understanding, but other lectures are in English, French and German.

The opening article on liquid–liquid extraction by H. IRVING and R. J. P. WILLIAMS (in Italian) is a thorough discussion of the theory and practice of this technique, and as such, is a most useful review of the subject. ENRICO CERRAI's paper on liquid ion exchangers (in Italian) describes in an elegant manner the new concept in chromatographic procedures which this technique introduces, and must be regarded as a classical paper on this subject. The role which adsorption plays in the behaviour of inorganic compounds on paper is reviewed by M. LEDERER from the point of view of paper electrophoresis, paper chromatography with organic solvents, radiochemistry, and the use of adsorption chromatography for analytical purposes, and indicates LEDERER's active interest in this field of work. The description by G. ALBERTI (in Italian), of the separation of inorganic cations on paper impregnated with either zirconium phosphate, or ammonium molybdophosphate is an informed account of the

work that has been done in applying these ideas to groups of metals including the rare earths. A summary of A. T. JAMES' lecture on gas–liquid chromatography is included; this makes no reference to the separation of inorganic compounds, but relates more to the technique of GLC. No one is a greater enthusiast for high voltage electrophoresis than D. GROSS, and his account of the applications to the separation of alkali metals, alkaline earths and heavy metals, inorganic acids, and phosphorus acids reveals the potentiality and speed of separation which this technique can achieve. A most stimulating review by E. BLASIUS (in German) of some special aspects of complex salts and their separation is given here with extreme thoroughness, and represents a unique discussion of this interesting research field.

The comprehensive survey of the chromatography of condensed phosphates and other polyanions by J. P. EBEL (in French) illustrates the vital importance of chromatographic techniques of all kinds in separating compounds with closely similar chemical properties, and without which the chemistry of phosphorus could not advance. Radio-chromatography in the gas phase is not very well known or much practised, and for this reason alone, one finds the final article (in French) in this volume, by J.-P. ADLOFF, an adequate introduction to a new procedure which has further potential applications, especially in biochemical research.

In Volume II, C. G. CASINOVI (in Italian) discusses counter current extraction processes from the theoretical point of view, but he does not give any inorganic applications, which indicates the paucity of information in this field. The techniques and principles of partition chromatography of metal ions and anions, together with an original scheme of analysis of cation mixtures by paper chromatography, and discussions on the separations of rare earths and other applications to the inorganic field, are presented by F. H. POLLARD. In contrast to the high voltage work of GROSS, a review of low voltage electrophoresis by G. DE ANGELIS (in Italian) provides an account of the more usual application of this technique to inorganic separations of all kinds. Quantitative determinations by radiochromatography is the subject of a chapter by POCCHIARI AND ROSSO (in Italian) who show how this technique can be applied experimentally.

The standard of presentation of material in these volumes is very high, and the coloured illustrations which make some of the articles most attractive and realistic are especially good. For those not familiar with the advances that have been made in the separation of inorganic compounds, these books will provide stimulating reading, and may suggest ways and means of solving some tantalising problems of chemistry.

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BOOK REVIEWS

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