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PROVISIONAL

INTERNATIONAL UNION OF PURE
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ANALYTICAL CHEMISTRY DIVISION

COMMISSION ON ELECTROANALYTICAL CHEMISTRY

# RECOMMENDED TERMS, SYMBOLS, AND DEFINITIONS FOR ELECTROANALYTICAL CHEMISTRY

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Comments on these proposals should be sent within 8 months
of publication to the Secretary of the Commission:

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Comments from the viewpoint of languages other than English are encouraged. These may have special significance regarding the eventual publication in various countries of translations of the nomenclature finally approved by IUPAC.

PROVISIONAL

Analytical Chemistry Division

Commission on Electroanalytical Chemistry

# RECOMMENDED TERMS, SYMBOLS, AND DEFINITIONS FOR ELECTROANALYTICAL CHEMISTRY[†]

## INTRODUCTION

This document contains definitions and recommendations for terminology and the usage of symbols in electroanalytical chemistry. Its scope is the same as that of the 1975 rules on "Classification and Nomenclature of Electroanalytical Techniques," [*Pure and Appl. Chem.*, *45* (1976) 81-97] and it supplements that document by giving explanations and definitions of the terms and symbols associated with the electroanalytical techniques there classified and named. The names given to specific techniques here are accompanied by numbers [e.g., "(4.21)"] that serve as cross-references to that document. Such numbers are always enclosed in parentheses.

Some of those techniques, including conductometry and potentiometry among others, are important to scientists in other areas as well as to electroanalytical chemists, and many terms, definitions, and symbols appropriate to such techniques may be found in Appendix III to the *Manual of Symbols and Terminology for Physicochemical Quantities and Units* [*Pure and Appl. Chem.*, *37*(4) (1974), 501] prepared by R. Parsons for Commission I.3 on Electrochemistry. Since material contained in Appendix III has not been duplicated here, both documents are needed to provide a complete list of the recommended terms, symbols, and definitions that are of importance to electroanalytical chemists. Some cross-references to Appendix III are given in the second column below and are always enclosed in square brackets; for example, the entry "[2.1]" under "n" below refers to the definition of "charge number of the cell reaction" in Appendix III.

The terms listed in this document are given in alphabetical order, and each is given a number for ease of cross-reference. Many of the terms are accompanied by two or more symbols. The first of these is always the recommended one; any other not enclosed in parentheses is considered to be an acceptable alternative. Parentheses are used to denote symbols which have often been used in the past but of which the future use should be discouraged.

The use of the symbol $I$ to denote electric current has been recommended by the Union and other international scientific organizations. The lower case $i$ is preferred here, not only because it has been (and continues to be) far more widely used in the electroanalytical literature, but also to avoid confusion with the polarographic diffusion current constant (*q.v.*), which has always been denoted by the symbol $I$. It may be hoped that electroanalytical chemists will eventually adopt the symbol $I$ to denote electric current. This would be facilitated by using the symbol $\mathcal{J}$ to denote the polarographic diffusion current constant and similarly using script capital letters to denote the fundamental response constants of other techniques — such as the chronocoulometric, chronopotentiometric, and voltammetric constants (*q.v.*).

For each recommendation the appropriate SI unit is given. Multiples and submultiples of these units are equally acceptable, and are often more convenient. For example, although the SI unit of concentration is mol $m^{-3}$, concentrations are frequently expressed in mol $dm^{-3}$, mol $cm^{-3}$, or mmol $dm^{-3}$. Similarly, although the SI unit of the chronopotentiometric constant defined below is A $s^{1/2}$ $mol^{-1}$ m, nearly all of the chronopotentiometric constants reported in the literature employ the practical unit mA $s^{1/2}$ $cm^{-2}$ (mol $dm^{-3})^{-1}$, or A $s^{1/2}$ $mmol^{-1}$ cm.

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| Recommended name and symbol; SI unit | Definition and remarks |
|---|---|
| 1. Apex | See "12. Current, apex." |
| 2. Area (of an electrode-solution interface)<br>$A$<br>$\mathrm{m^2}$<br>[5.7] | In these definitions the area of an electrode-solution interface is understood to be the geometrical or projected area, and to ignore surface roughness. |
| 3. Characteristic potential<br>(no symbol recommended)<br>V | An applied potential that is characteristic of a charge-transfer process and the experimental conditions (such as the composition of the solvent and supporting electrolyte and the temperature) under which it is investigated, and whose nature depends on the technique that is employed. Some typical characteristic potentials are the half-wave potential (*cf.* 60) in polarography (5.12), the quarter-transition-time potential (*cf.* 62) in chronopotentiometry (4.12), the peak potential (*cf.* 61) and the half-peak potential (*cf.* 59) in linear-sweep voltammetry (5.8), and the summit potential (*cf.* 63) in ac polarography (6.4). |
| 4. Chronocoulometric constant<br>$\mathcal{Q}$(script capital Q)<br>$\mathrm{A\ s^{1/2}\ mol^{-1}\ m}$ | In chronocoulometry (4.12), the empirically evaluated quantity defined by the equation<br>$\mathcal{Q} = \frac{1}{A\,c}\left(\frac{\Delta Q}{\Delta t^{1/2}}\right)$<br>where $A$ = area of the electrode-solution interface (*cf.* 2), $c$ = bulk concentration (*cf.* 6) of the electroactive substance, and $\Delta Q/\Delta t^{1/2}$ = the slope of a plot of $Q$ against $t^{1/2}$. |
| 5. Chronopotentiometric constant<br>$\mathcal{T}$ (script capital T)<br>$\mathrm{A\ s^{1/2}\ mol^{-1}\ m}$ | In chronopotentiometry (at constant current density) (4.12), the empirically evaluated quantity defined by the equation<br>$\mathcal{T} = i\,\tau^{1/2}/A\,c\ (= j\,\tau^{1/2}/c)$<br>where $i$ = electric current (cf. 7), $\tau$ = transition time (*cf.* 77), $A$ = area of the electrode-solution interface (*cf.* 2), $c$ = bulk concentration (*cf.* 6) of the electroactive substance, and $j$ = current density = $i/A$. |
| 6. Concentration, bulk<br>$c_B$ ([B])<br>$\mathrm{mol\ m^{-3}}$ | In any technique that involves the establishment of a concentration gradient, either within the material from which an electrode is made or in the solution that is in contact with an electrode, the bulk concentration of a substance B is the total or analytical concentration of B at points so remote from the electrode-solution interface that the concentration gradient for B is indistinguishable from zero at the instant under consideration. In common practice the bulk concentration of B is taken to be the total or analytical concentration of B that would be present throughout the electrode or solution if there were no current flowing through the cell and if the electrode and solution did not interact in any way. In the absence of any homogeneous reaction or other process that produces or consumes B, the bulk concentration of B is the total or analytical concentration of B that is present before the excitation signal is applied. |

| Recommended name and symbol; SI unit | Definition and remarks |
|---|---|
| 7. Current (electric)<br>$i$, $I$<br>A<br>[8.1] | Attention is called to this Commission's Recommendations for Sign Conventions and Plotting of Electrochemical Data [Pure and Appl. Chem., 45 (1976)131], which describes the consequences for electroanalytical chemistry of a recently adopted convention regarding the sign of the electric current. |
| 8. Current, adsorption<br>$i_{ads}$, $I_{ads}$<br>A | A faradaic current whose magnitude depends on the applied potential, and, at any particular applied potential, on the rate or extent of the adsorption of an electroactive substance (or the product obtained from the reduction or oxidation of an electroactive substance) onto the surface of the indicator or working electrode. See "9. Current, limiting adsorption." |
| 9. Current, limiting adsorption<br>$i_{ads,\ell}$, $I_{ads,\ell}$<br>A<br>[8.3] | The potential-independent value that is approached by an adsorption current as the rate of reduction or oxidation of the electroactive substance is increased by varying the applied potential.<br>The terms "adsorption current" and "limiting adsorption current" should not be applied to faradaic currents that have been increased or decreased by adding a non-electroactive surfactant to a solution containing an electroactive substance, nor to apparent waves resulting from the effect of adsorption or desorption on double-layer currents. |
| 10. Current, alternating<br>$i_{ac}$, $I_{ac}$<br>A | This term should be reserved for sinusoidal wave forms; all other wave forms should be termed "periodic." |
| 11. Current, alternating, amplitude of<br>$i_{ac}$, $I_{ac}$<br>A | This term should denote half of the peak-to-peak amplitude of the sinusoidal alternating current. |
| 12. Current, apex<br>$i_{ap}$, $I_{ap}$<br>A | In measurement of non-faradaic admittance (or tensammetry) (3.2), a plot of alternating current against applied potential shows a minimum or maximum when a non-electroactive substance undergoes adsorption or desorption at the surface of the indicator electrode. Such a maximum or minimum may be called an "apex" to emphasize its non-faradaic origin and distinguish it from a "summit," which would result from a charge-transfer process. The highest value of the current on such an apex may be called an "apex current," and the corresponding applied potential may be called an "apex potential." |
| 13. Current, capacity | See "20. Current, double-layer." |
| 14. Current, catalytic<br>$i_{cat}$, $I_{cat}$<br>A | The faradaic current that is obtained with a solution containing two substances B and A may exceed the sum of the faradaic currents that would be obtained with B and A separately, but at the same concentrations and under the same experimental conditions. In either of the two following situations the increase is termed a "catalytic current." |

| Recommended name and symbol; SI unit | Definition and remarks |
|---|---|
| | 14.1. B is reduced or oxidized at the electrode-solution interface to give a product B' that then reduces or oxidizes A chemically. The reaction of B' with A may yield either B or an intermediate in the overall half-reaction by which B' was obtained from B. In this situation the increase of current that results from the addition of A to a solution of B may be termed a "regeneration current."<br>14.2. The presence at the electrode-solution interface of one substance, which may be either A or the product A' of its reduction or oxidation, decreases the over-potential for the reduction or oxidation of B.<br>In either case the magnitude of the catalytic current depends on the applied potential.<br>14.3. If the current observed with a mixture of A and B is smaller than the sum of the separate currents, the term "non-additive current" should be used. |
| 15. Current, limiting catalytic<br>$i_{\mathrm{cat},\ell}$ , $I_{\mathrm{cat},\ell}$<br>A<br>[8.3] | The potential-independent value that is approached by a catalytic current as the rate of the charge-transfer process is increased by varying the applied potential. |
| 16. Current, charging | See "20. Current, double-layer." |
| 17. Current, diffusion (-controlled)<br>$i_d$, $I_d$<br>A | A faradaic current whose magnitude is controlled by the rate at which a reactant in an electrochemical process diffuses toward an electrode-solution interface (and, sometimes, by the rate at which a product diffuses away from that interface).<br>For the reaction mechanism<br>$C \underset{k_-}{\overset{k}{\rightleftharpoons}} B \xrightarrow{+ne} B'$<br>there are two common situations in which a diffusion current can be observed. In one, the rate of formation of B from electroinactive C is small and the current is governed by the rate of diffusion of B toward the electrode surface. In the other, C predominates at equilibrium in the bulk of the solution, but its transformation into B is fast; C diffuses to the vicinity of the electrode surface and is there rapidly converted into B, which is reduced. |
| 18. Current, limiting diffusion<br>$i_{d,\ell}$, $I_{d,\ell}$<br>A<br>[8.3] | The potential-independent value that is approached by a diffusion current as the rate of the charge-transfer process is increased by varying the applied potential. |
| 19. Current, direct<br>$i_{dc}$, $I_{dc}$<br>A | This term and its symbol should be used (in preference to "current" alone) only to denote the steady (time-independent) component of a current that also has a periodic component. |

| Recommended name and symbol; SI unit | Definition and remarks |
|---|---|
| 20. Current, double-layer<br>$i_{DL}$, $I_{DL}$<br>A | The non-faradaic current associated with the charging of the electrical double layer at an electrode-solution interface, given by $i_{DL} = d(\sigma A)/dt$ where $\sigma$ = surface charge density of the double layer [5.2], $A$ = area of the electrode-solution interface (*cf.* 2), and $t$ = time.<br>Capital letters should be used as subscripts to avoid the possibility of confusing this symbol with that for the limiting diffusion current (*cf.* 18). |
| 21. Current, faradaic<br>(no symbol recommended)<br>A | A current corresponding to the reduction or oxidation of some chemical substance. |
| 22. Current, net faradaic<br>(no symbol recommended)<br>A | The algebraic sum of all the faradaic currents flowing through an indicator or working electrode. |
| 23. Current, faradaic demodulation<br>$i_{FD}$, $I_{FD}$<br>A | A component of the current that is due to the demodulation associated with an electrode reaction and that appears if an indicator or working electrode is subjected to the action of two intermodulated applied potentials of different frequency. |
| 24. Current, faradaic rectification<br>$i_{FR}$, $I_{FR}$<br>A | A component of the current that is due to the rectifying properties of an electrode reaction and that appears if an indicator or working electrode is subjected to any periodically varying applied potential while the mean value of the applied potential is controlled. |
| 25. Current, instantaneous<br>$i_t$, $I_t$<br>A | 25.1. At a dropping electrode, the total current that flows at the instant when a time $t$ has elapsed since the fall of the preceding drop.<br>25.2. At any other electrode, the total current that flows at the instant when a time $t$ has elapsed since the beginning of an electrolysis.<br>The instantaneous current is usually time-dependent and may have the character of an adsorption, catalytic, diffusion, double-layer, or kinetic current, and may include a migration current. A plot of the dependence of instantaneous current on time is commonly called an "$i$-$t$ curve." |
| 26. Current, kinetic<br>$i_k$, $I_k$<br>A | A faradaic current that corresponds to the reduction or oxidation of an electroactive substance B formed by a prior chemical reaction from another substance Y that is not electroactive, and that is partially or entirely controlled by the rate of that reaction. The reaction may be heterogeneous, occurring at an electrode-solution interface (surface reaction), or it may be homogeneous, occurring at some distance from the interface (volume reaction). See also "17. Current, diffusion." |

| Recommended name and symbol; SI unit | Definition and remarks |
|---|---|
| 27. Current, limiting kinetic<br>$i_{k,\ell}$, $I_{k,\ell}$<br>A<br>[8.3] | The potential-independent value that is approached by a kinetic current as the rate of the charge-transfer process is increased by varying the applied potential. |
| 28. Current, limiting<br>$i_{\ell}$, $I_{\ell}$<br>A<br>[8.3] | A limiting current is the limiting value of a faradaic current that is approached as the rate of the charge-transfer process is increased by varying the potential. It is independent of the applied potential over a finite range, and is usually evaluated by subtracting the appropriate residual current from the measured total current. A limiting current may have the character of an adsorption, catalytic, diffusion, or kinetic current, and may include a migration current. |

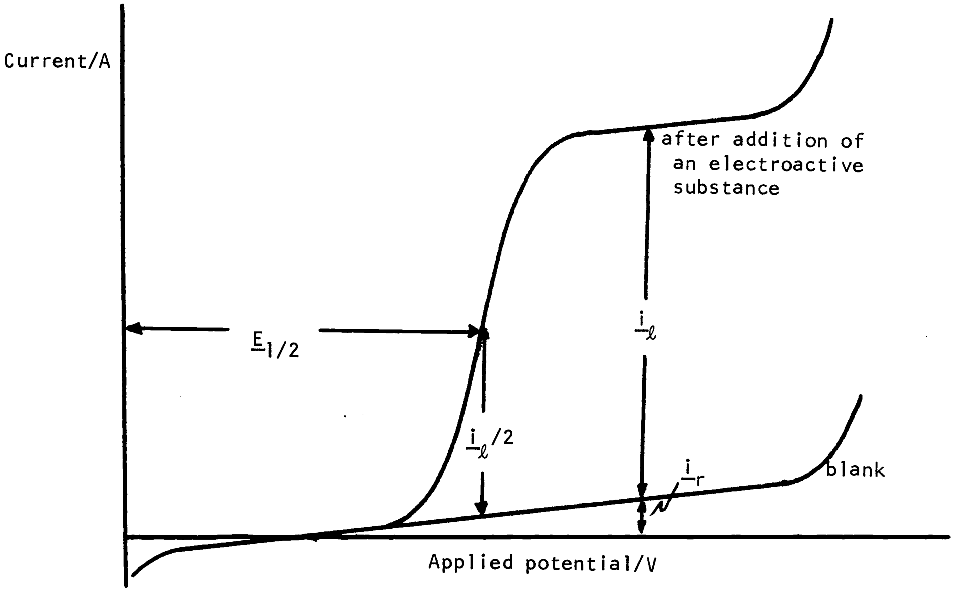

Fig. 1. Idealized polarogram, illustrating the limiting current $i_{\ell}$, the residual current $i_r$, and the half-wave potential $E_{1/2}$.

| Recommended name and symbol; SI unit | Definition and remarks |
|---|---|
| 29. Current, migration<br>$i_m$, $I_m$<br>A | The difference between the current that is actually obtained, at any particular value of the potential of the indicator or working electrode, for the reduction or oxidation of an ionic electroactive substance and the current that would be obtained, at the same potential, if there were no transport of that substance due to the electric field between the electrodes. The sign convention regarding current is such that the migration current is negative for the reduction of a cation or for the oxidation of an anion, and positive for the oxidation of a cation or the reduction of an anion. Hence the migration current may tend to either increase or decrease the total current observed. In any event the migration current approaches zero as the transport number of the electroactive substance is decreased by increasing the concentration of the supporting electrolyte, and hence the conductivity. |

| Recommended name and symbol; SI unit | Definition and remarks |
|---|---|
| 30. Current, limiting migration<br>$i_{m,\ell}$, $I_{m,\ell}$<br>A<br>[8.3] | The limiting value of a migration current, which is approached as the rate of the charge-transfer process is increased by varying the applied potential. |
| 31. Current, non-additive | See "14(.3) Catalytic current." |
| 32. Current, peak<br>$i_p$, $I_p$<br>A | In linear-sweep voltammetry (5.8), triangular-wave voltammetry (5.19), cyclic triangular-wave voltammetry (5.21), and similar techniques, the maximum value of the faradaic current due to the reduction or oxidation of a substance B during a single sweep. This maximum value is attained after an interval during which the concentration of B at the electrode-solution interface decreases monotonically, while the faradaic current due to the reduction or oxidation of B increases monotonically, with time. It is attained before an interval during which this current decreases monotonically with time because the rate of transport of B toward the electrode-solution interface is smaller than the rate at which it is removed from the interface by electrolysis. |

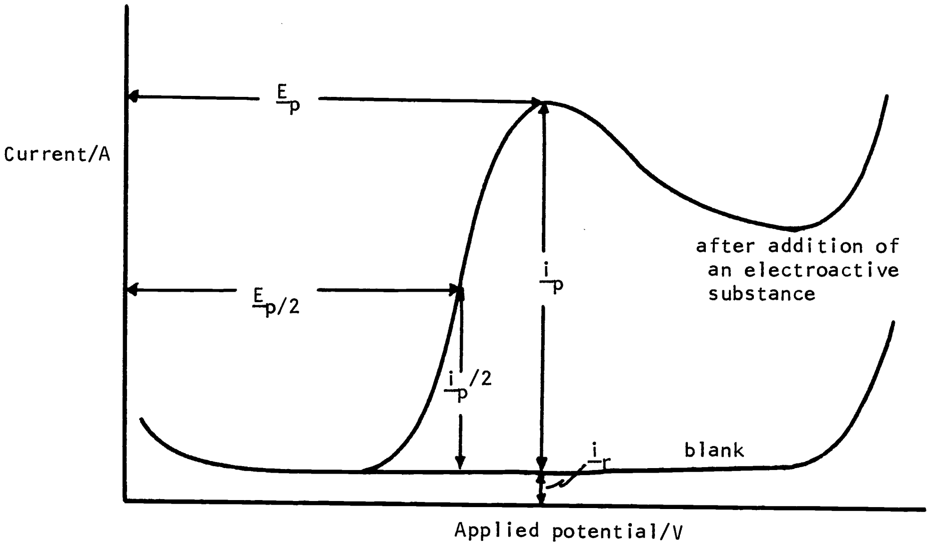

Fig. 2. Idealized linear-sweep voltammogram, illustrating the peak current $i_p$, the residual current $i_r$, the peak potential $E_p$, and the half-peak potential $E_{p/2}$.

The term "peak current" has also been used to denote the maximum value of the faradaic current attributable to the reduction or oxidation of an electroactive substance in techniques such as ac polarography (6.4), differential pulse polarography (6.3), and derivative polarography (5.13). However, these techniques give curves that arise in ways different from that cited above, and the terms "summit," "summit current," and "summit potential" are therefore recommended for use in connection with such techniques. See also "12. Current, apex."

| Recommended name and symbol; SI unit | Definition and remarks |
|---|---|
| 33. Current, periodic | See "10. Current, alternating." |
| 34. Current, regeneration | See "14(.1) Current, catalytic." |
| 35. Current, residual<br>$i_r$, $I_r$<br>A | The current that flows, at any particular value of the applied potential, in the absence of the substance whose behavior is being investigated (*i.e.*, in a blank solution). See Figs. 1-3. |
| 36. Current, square-wave<br>$i_{SW}$, $I_{SW}$<br>A | In square-wave polarography (6.5), the component of the current that is associated with the presence of a substance B. This component may be either faradaic (if B is electroactive) or non-faradaic (if B is surface-active). |
| 37. Current, summit<br>$i_{su}$, $I_{su}$<br>A | In ac polarography (6.4), differential pulse polarography (6.3), derivative polarography (5.13), square-wave polarography (6.5), and similar techniques, the maximum value of the component of the current that is associated with the presence of a substance B. Normally this component of the current is faradaic, and the maximum arises because the rate of variation (with applied potential) of the rate of the charge-transfer process passes through a maximum. Similar maxima arise when this component is non-faradaic (and when B is surface-active rather than electroactive). In a case known to be of the latter type, the term "apex current" is recommended as being more specific. |

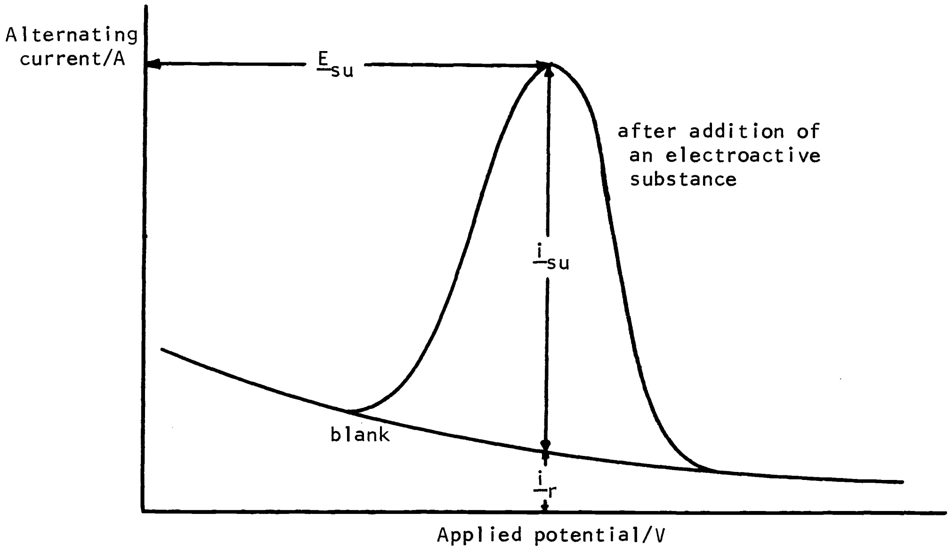

Fig. 3. Idealized ac polarogram, illustrating the summit current $i_{su}$, the residual current $i_r$, and the summit potential $E_{su}$.

| Recommended name and symbol; SI unit | Definition and remarks |
|---|---|
| 38. Depolarizer | The term "electroactive substance" (*cf.* 41) should be used in preference to "depolarizer." |
| 39. Diffusion current constant<br>$I$, $\mathcal{I}$ (script capital I)<br>A $\mathrm{mol}^{-1}$ $\mathrm{m}^3$ $\mathrm{kg}^{-2/3}$ $\mathrm{s}^{1/2}$ | In polarography (5.12), the empirical quantity defined by the equation<br>$I = i_{d,\ell}/c_B m^{2/3} t_1^{1/6}$<br>where $i_{d,\ell}$ = limiting diffusion current (*cf.* 18), $c_B$ = bulk concentration of the substance B whose reduction or oxidation is responsible for the wave in question (*cf.* 6), $m$ = average rate of (mass) flow of mercury (or other liquid metal) (*cf.* 67) and $t_1$ = drop time (*cf.* 40). |
| 40. Drop time<br>$t_1$, $\tau$, $t_d$<br>s | In polarography (5.12), the time that elapses between the instants at which two successive drops of liquid metal are detached from the tip of the capillary. |
| 41. Electroactive substance | 41.1 In voltammetry and related techniques, a substance that undergoes a change of oxidation state, or the breaking or formation of chemical bonds, in a charge-transfer step.<br>If an electroactive substance B is formed, in the solution or electrode, by a chemical reaction from another substance C, the substance C should be called the precursor of B.<br>41.2. In potentiometry with ion-selective electrodes, a material containing, or in ion-exchange equilibrium with, the sensed ion. The electroactive substance is often incorporated in an inert matrix such as poly(vinyl)-chloride or silicone rubber. |
| 42. Electrode, auxiliary | Three-electrode cells comprise (1) an indicator (or test) electrode (*cf.* 44) or a working electrode (*cf.* 47), at the surface of which processes that are of interest may occur, (2) a reference electrode (*cf.* 45), and (3) a third electrode, the auxiliary or counter electrode, which serves merely to carry the current flowing through the cell, and at the surface of which no processes of interest occur.<br>If processes of interest occur at both the anode and the cathode of a cell [as in differential amperometry (4.17) or controlled-current potentiometric titration with two indicator electrodes (4.11)], the cell should be said to comprise two indicator (or test) or working electrodes. |
| 43. Electrode, counter | See "42. Electrode, auxiliary." |
| 44. Electrode, indicator | An electrode that serves as a transducer responding to the excitation signal (if any) and to the composition of the solution being investigated, but that does not effect an appreciable change of bulk composition within the ordinary duration of a measurement. |

| Recommended name and symbol; SI unit | Definition and remarks |
|---|---|
| 45. Electrode, reference | An electrode that maintains a virtually invariant potential under the conditions prevailing in an electrochemical measurement, and that serves to permit the observation, measurement, or control of the potential of the indicator (or test) or working electrode. |
| 46. Electrode, test | See "44. Electrode, indicator." |
| 47. Electrode, working | An electrode that serves as a transducer responding to the excitation signal and the concentration of the substance of interest in the solution being investigated, and that permits the flow of current sufficiently large to effect appreciable changes of bulk composition within the ordinary duration of a measurement. |
| 48. Electrolyte, base | See "50. Electrolyte, supporting." |
| 49. Electrolyte, indifferent | See "50. Electrolyte, supporting." |
| 50. Electrolyte, supporting | 50.1. An electrolyte solution, whose constituents are not electroactive in the range of applied potentials being studied, and whose ionic strength (and, therefore, contribution to the conductivity) is usually much larger than the concentration of an electroactive substance to be dissolved in it.<br>50.2. The solutes that are present in such a solution. |
| 51. Frequency<br>Hz | It is essential to draw a careful distinction between the electrical frequency of an excitation signal or measured response and the rate of rotation of a rotating disc, wire, or other electrode. |
| 52. Mass-transfer-controlled electrolyte rate constant<br>$s_B$<br>$s^{-1}$ | In controlled-potential coulometry (4.27) and related techniques, the empirically evaluated constant of proportionality defined by the equation<br>$s_B = -(1/c_B)(dc_B/dt)$<br>where $c_B$ is the bulk concentration (*cf.* 6) of the substance B, and $dc_B/dt$ is the rate of change of that concentration, resulting from the consumption of B by reduction or oxidation at the working electrode. |
| 53. $n$<br>dimensionless<br>[1.2] | A stoichiometric ratio equal to the total number of electrons transferred between an electrode and a solution in the reduction or oxidation of one ion or molecule of an electroactive substance, whose identity must be specified. No other substance that is initially present may be reduced or oxidized during the process (see "14. Current, catalytic"). |
| 54. $n_{app}$<br>dimensionless | An experimentally measured quantity equal to the total number of electrons transferred between an electrode and a solution in consequence of the oxidation or reduction of one ion or molecule of an electroactive substance, whose identity must be specified. |

| Recommended name and symbol; SI unit | Definition and remarks |
|---|---|
| | When the reduction or oxidation of a substance B is accompanied by chemical processes such as the catalyzed or induced reduction of a second substance, or a side reaction that consumes B or an intermediate, the value of $n_{app}$ will differ from that of $n$ (*cf.* 53). |
| 55. Outflow velocity (of mercury or other liquid metal) | See "67 (and 68). Rate of flow." |
| 56. Peak | See "32. Current, peak." |
| 57. Potential, apex | See "12. Current, apex." |
| 58. Potential, applied<br>$E_{app}$<br>V<br>[2.2] | The difference of potential measured between identical metallic leads to two electrodes of a cell. The applied potential is divided into two electrode potentials, each of which is the difference of potential existing between the bulk of the solution and the interior of the conducting material of the electrode, an $iR$ or ohmic potential drop through the solution, and another ohmic potential drop through each electrode.<br>In the electroanalytical literature this quantity has often been denoted by the term "voltage," whose continued use is not recommended. |
| 59. Potential, half-peak<br>$E_{p/2}$<br>V | In linear-sweep voltammetry (5.8), triangular-wave voltammetry (5.19), cyclic triangular-wave voltammetry (5.21), and similar techniques, the potential of the indicator electrode at which the difference between the total current and the residual current is equal to one-half of the peak current (*cf.* 32). This potential is attained in the interval in which the rate of the charge-transfer process, and hence the (absolute value of the) current, increase monotonically with time. See Fig. 2. |
| 60. Potential, half-wave<br>$E_{1/2}$<br>V | The potential of a polarographic or voltammetric indicator electrode at the point, on the rising part of a polarographic or voltammetric wave, where the difference between the total current and the residual current is equal to one-half of the limiting current (*cf.* 28). See Fig. 1. The quarter-wave potential $E_{1/4}$, the three-quarter-wave potential $E_{3/4}$, etc., may be similarly defined. |
| 61. Potential, peak<br>$E_p$<br>V | In linear-sweep voltammetry (5.8), triangular-wave voltammetry (5.19), cyclic triangular-wave voltammetry (5.21), and similar techniques, the potential of the indicator electrode at which the peak current (*cf.* 32) is attained. See Fig. 2. |
| 62. Potential, quarter-transition-time<br>$E_{\tau/4}$<br>V | In chronopotentiometry (at constant current density) (4.12), the potential of the indicator electrode at the instant when the time that has elapsed since the application of current is equal to one-fourth of the transition time (*cf.* 7). Appropriate correction for double-layer charging phenomena is needed in practice. |

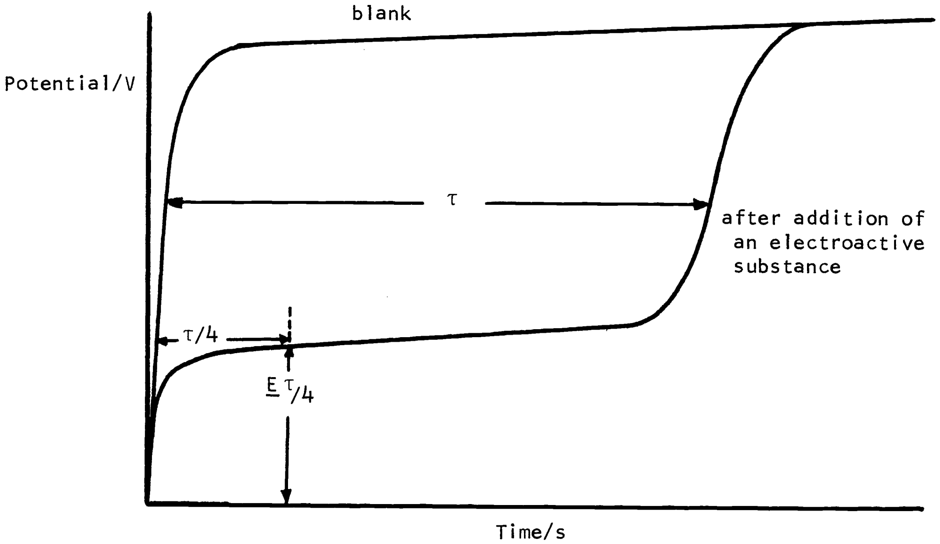

Fig. 4. Idealized chronopotentiogram, illustrating the quarter-transition-time potential $E_{\tau/4}$ and the transition time τ.

| Recommended name and symbol; SI unit | Definition and remarks |
|---|---|
| 63. Potential, summit<br>$E_{su}$<br>V | In ac polarography (6.4), differential pulse polarography (6.3), derivative polarography (5.13), and similar techniques, the potential of the indicator electrode at which the summit current (*cf.* 37) is attained. See Fig. 3. |
| 64. Precursor (of an electroactive substance) | See "41. Electroactive substance." |
| 65. Pulse duration<br>$t_p$<br>s | In pulse polarography (5.22), differential pulse polarography (6.3), Kalousek polarography (5.24), and related techniques, the duration of an interval during which the excitation signal deviates from the base line. This interval includes the sampling interval (*cf.* 72). |
| 66. Quantity of electricity<br>$Q$<br>C | The quantity of electricity that flows during the interval between $t_1$ and $t_2$ is given by<br>$Q = \int_{t_1}^{t_2} i_t dt$<br>where $i_t$ is the instantaneous current at any instant during that interval. The reduction of an electroactive substance gives rise to negative values of $Q$; the oxidation of an electroactive substance gives rise to positive values of $Q$. The components of an overall value of $Q$ should be named and given symbols similar to those of the corresponding currents, *e.g.*, $Q_{DL}$ = double-layer quantity of electricity, $Q_t$ = instantaneous quantity of electricity, etc. |
| 67. Rate of flow (or mercury or other liquid metal), average<br>$m$<br>kg s$^{-1}$ | In polarography (5.12), the ratio of the mass of a drop, at the instant when it is detached from the tip of the capillary, to the drop time $t_1$ (*cf.* 40); the average value of the instantaneous rate of flow over the entire life of the drop. |

| Recommended name and symbol; SI unit | Definition and remarks |
|---|---|
| 68. Rate of flow (or mercury or other liquid metal), instantaneous<br>$m_t$<br>kg s$^{-1}$ | In polarography (5.12), the rate of increase of the mass of a drop at a particular instant $t$ seconds after it has begun to form. |
| 69. Reaction, surface | See "26. Current, kinetic." |
| 70. Reaction, volume | See "26. Current, kinetic." |
| 71. Response constant<br>(no symbol recommended) | A quantity whose expression includes a current, whose value is characteristic of a charge-transfer process and the experimental conditions under which it is investigated, and whose nature depends on the technique that is employed. Some typical response constants are the diffusion current constant (*cf.* 39) in polarography (5.12), the voltammetric constant (*cf.* 82) in linear-sweep voltammetry (5.8), and the chronopotentiometric constant (*cf.* 5) in chronopotentiometry (4.12). |
| 72. Sampling interval | In Tast polarography (5.15), square-wave polarography (6.5), and similar techniques, the interval during which the current is measured or recorded. |
| 73. Sampling time<br>$t_m$<br>s | In Tast polarography (5.15), square-wave polarography (6.5), and similar techniques, the duration of the sampling interval (*cf.* 72). |
| 74. Strobe interval | [In Tast polarography (5.15)] See "73. Sampling time." |
| 75. Tast interval | [In Tast polarography (5.15)] See "73. Sampling time." |
| 76. Thickness of the reaction layer<br>$\mu$<br>m | When a kinetic current (*cf.*26) flows, the concentrations of the electroactive substance B and its precursor C at very small distances from the electrode surface are influenced both by mass transfer and by the finite rate of establishment of the chemical equilibrium. As the distance from the electrode surface increases, the chemical equilibrium is more and more nearly attained. The thickness of the reaction layer is the distance from the electrode surface beyond which deviations from the chemical equilibrium between C and B are taken to be negligibly small. |
| 77. Transition time<br>$\tau$<br>s | In chronopotentiometry (4.12) and related techniques, the time that elapses between the instant at which current is applied and the instant at which the concentration of an electroactive substance B at the electrode-solution interface becomes indistinguishable from zero. In experimental practice the latter time is often taken to be the instant at which the rate of variation of the potential of the indicator electrode attains a maximum value. See Fig. 4. |

| Recommended name and symbol; SI unit | Definition and remarks |
|---|---|
| 78. Voltage<br>$e$<br>V | The use of this term is discouraged, and the term "applied potential" should be used instead, for non-periodic signals. However, it is retained here for sinusoidal and other periodic signals because no suitable substitute for it has been proposed. |
| 79. Voltage, alternating<br>$e_{ac}$<br>V | This term should be applied only to sinusoidal phenomena; the term "periodic voltage" should be used for other wave forms. |
| 80. Voltage, alternating, amplitude<br>$e_{ac}$<br>V | This term should denote half of the peak-to-peak amplitude. Peak-to-peak and r.m.s. amplitudes should be so specified. |
| 81. Voltage, periodic<br>$e_{pc}$<br>V | This general term is applicable to square, triangular, and other wave forms; the term "alternating voltage" should be reserved for sinusoidal wave forms. |
| 82. Voltammetric constant<br>$\mathcal{V}$ (script capital V)<br>$\mathrm{A\ mol^{-1}\ V^{-1/2}\ m\ s^{1/2}}$ | In linear-sweep voltammetry (5.8) and related techniques, the empirical quantity defined by the equation<br>$\mathcal{V} = i_p/Av^{1/2}\ c_B\ (= j_p/v^{1/2}c_B)$<br>where $i_p$ = peak current (*cf.* 32), $A$ = area of the electrode-solution interface (cf. 2), $v$ = rate of change of applied potential, and $c_B$ = bulk concentration of the substance B whose reduction or oxidation is responsible for the peak in question (*cf.* 6). |
| 83. Wave height | The limiting current (*cf.* 28) of an individual wave, frequently expressed in arbitrary units for convenience. |