8.4 General terms, symbols and definitions used in electroanalytical chemistry

The fundamental terms can be found in Chapter 1 and 2, while the specific subjects in the corresponding subsections (8.2, 8.3 and 8.5). Each term is followed by the recommended symbol and its SI unit.

Activity, a

Activity coefficient, f (γ_m, γ_c)

See also sections 1.3.8 and 3.3.

Anode, (no symbol recommended)

An electrode of a cell at which an electroactive substance is electrooxidized.

Area (of an electrode-solution interface), A; m^2

The area of the electrode-solution interface is understood to be the geometrical or projected area, with surface roughness being ignored.

Cathode, (no symbol recommended)

An electrode of a cell at which an electroactive substance is electroreduced.

Characteristic potential (no symbol recommended); V

An applied potential that is characteristic of a charge-transfer or an adsorption process and the experimental conditions (such as the composition of the solvent and supporting electrolyte and 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* in polarography, the *quarter transition-time potential* in chronopotentiometry, the *peak potential* and the *half-peak potential* in linear sweep voltammetry, and the *summit potential* in ac polarography.

Charge, electric, Q; C

See *quantity of electricity*, in section 1.3.3.

Chronocoulometric constant, Q; A s$^{1/2}$ mol^{-1} m

In *chronocoulometry*, the empirically determined quantity, defined by the equation

$$Q = \frac{1}{Ac}\left(\frac{\Delta Q}{\Delta t^{1/2}}\right)$$

where A is the area of the electrode-solution interface
                 c is the bulk concentration of the electroactive substance, and
$\Delta Q/\Delta t^{1/2}$ is the slope of a plot of Q against $t^{1/2}$.

Chronopotentiometric constant, T; A s$^{1/2}$ mol^{-1} m

In chronopotentiometry (at constant current density), the empirically evaluated quantity defined by the equation

$$T = i\tau^{1/2}/A\,c_B\ (=j\tau^{1/2}/c_B)$$

where i is the electric current,
              τ is the transition time,
              A is the area of the electrode-solution interface,
              c_B is the bulk concentration of the electroactive substance B, and
              $j = i/A$ is the current density.

Concentration, bulk, c_B ; mol m^{-3}

In any technique in which a concentration gradient is established, either within the electrode material or in the solution layer adjacent to an electrode surface, 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 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, i.e. there was no B adsorption on the electrode. 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 working electrode is immersed in solution.

Note: The use of [B] is discouraged.

Current (electric), i, I; A

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 the adopted convention regarding the sign of the electric current.

Current, adsorption, i_{ads}, I_{ads}; 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 working electrode.

Current, limiting adsorption, $i_{ads,l}, I_{ads,l}$; A

The potential-independent adsorption current that is attained by varying the applied potential as the rate of electroreduction or electrooxidation of the electroactive substance is larger than the rate of adsorption.

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.

Current, alternating, i_{ac}, I_{ac}; A

This term should be reserved for sinusoidal current wave forms; all other current wave forms repeated with time should be termed "periodic".

Current, alternating, amplitude of, i_{ac}, I_{ac}; A

This term should denote half of the peak-to-peak distance of the sinusoidal alternating current.

Current, apex, i_{ap}, I_{ap}; A

In measurement of non-faradaic admittance (or tensammetry), there is a minimum or maximum on a plot of alternating current against applied potential when a non-electroactive substance is adsorbed or desorbed on the surface of the working 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 current value

of such an apex may be called an *apex current*, and the corresponding applied potential may be called an *apex potential*.

Current, capacity

See *current, double-layer*.

Current, catalytic, i_{cat}, I_{cat}; A

The faradaic current measured in a solution containing two electroactive substances, A and B, may exceed the sum of the faradaic currents that would be obtained for A and B separately under the same experimental conditions. In either of the two following situations this current increase is termed a catalytic current.

(i)   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 case, the increase of current that results from the addition of A to a solution of B may be termed a *regeneration current*.

(ii)   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.

In either case, the magnitude of the catalytic current depends on the applied potential.
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.

Current, limiting catalytic, $i_{cat,l}$, $I_{cat,l}$; A

The potential-independent catalytic current that is attained by varying the applied potential as the rate of the charge-transfer is larger than the catalytic regeneration of an electroactive species.
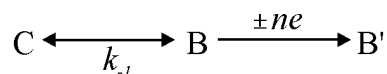

Current, charging

See *current, double-layer*.

Current, diffusion-controlled, i_d, I_d; A

A faradaic current whose magnitude is controlled by the rate at which an electroactive species diffuses toward an electrode-solution interface (and, sometimes, by the rate at which a product diffuses away from that interface).

For istance for the reaction mechanism:

$$C \xrightleftharpoons[k_{-1}]{} B \xrightarrow{\pm ne} B'$$

There are two main cases in which a diffusion current can be observed. In one, the rate of formation of B from electroinactive C is small but its transformation into B is fast; and the current is governed by the rate of diffusion of B at equilibrium in the bulk of the solution. In the other C diffuses to the vicinity of the electrode surface and it is there rapidly converted into B, which is then reduced.

Current, limiting diffusion, $i_{d,l}$, $I_{d,l}$; A

The potential-independent diffusion current that is attained by varying the applied potential as the rate of the charge-transfer process is larger than the diffusion rate.

Current, direct, i_{dc}, I_{dc}; 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 may have a periodic component.

Current, double-layer, i_{DL}, I_{DL}; A

The non-faradaic current associated with the charging of the electrical double layer at an electrode-solution interface, $i_{DL} = d(\sigma A)/dt$, where σ is the surface charge density of the double layer, A is the area of the electrode-solution interface, and t is the time.
Capital letters should be used as subscripts to avoid the possibility of confusing this symbol with that for the limiting diffusion current.

Current, faradaic; i_F, I_F, A

A current corresponding to the electroreduction or electrooxidation of an electroactive substance.

Current, net faradaic; A

The algebraic sum of all the faradaic currents flowing through a working electrode.

Current, faradaic demodulation, i_{FD}, I_{FD}; A

A current component that is due to the demodulation associated with an electrode reaction. It appears if two intermodulated potentials of different frequency are applied to a working electrode.

Current, faradaic rectification, i_{FR}, I_{FR}; A

A current component that is due to the rectifying properties of an electrode reaction. It appears if any periodically varying applied potential is applied to a working electrode, at the mean value of the applied potential being controlled.

Current, instantaneous, i_t, I_t; A

The total current at the instant when a time t has elapsed since the beginning of an electrolysis.

At a dropping electrode, the total current at the instant when the time t has elapsed since the fall of the preceding drop.

The instantaneous current is usually time-dependent and may have 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".

Current, kinetic, i_k, I_k; A

A faradaic current that corresponds to the electroreduction or electrooxidation of an electroactive substance B formed by a prior chemical reaction from another substance Y that is not electroactive. Kinetic current is partially or entirely controlled by the rate of the chemical reaction. This reaction may be heterogeneous, occurring at an electrode-solution interface (surface reaction), or it may be homogeneous, occurring at some distance from the interface (bulk reaction).

See also *Current, diffusion*.

Current, limiting kinetic, $i_{k,l}$, $I_{k,l}$; A

The potential-independent kinetic current that is attained by varying the applied potential as the rate of the charge-transfer process is larger than the rate of the chemical reaction.

Current, limiting, i_l, I_l; A

A limiting current is the limiting value of a faradaic current that is attained by varying the potential as the rate of the charge-transfer process is larger than the rate of the accompanying transport rate of the electroactive substance. It is independent of the applied potential over a finite range, and is usually edetermined by subtracting the appropriate residual current from the measured total current (Fig.8.4.1.). A limiting current may have the character of an adsorption, catalytic, diffusion, or kinetic current, and may include a migration current.

Current, migration, i_m, I_m; A

The difference between the current that is actually measured, at any particular value of the potential of the working electrode for the electroreduction or electrooxidation of an ionic electroactive substance and the current that would be measured under the same conditions, 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.

Current, limiting migration, $i_{m,l}$, $I_{m,l}$; A

The limiting value of a migration current, which is attained by varying the applied potential as the rate of the charge-transfer process is larger than the migration rate.

Current, non-additive

See *Catalytic Current*.

Current, peak, i_P, I_P; A

In linear-sweep voltammetry, triangular-wave voltammetry, cyclic triangular-wave voltammetry, and similar techniques, the maximum value of the faradaic current due to the electroreduction or electrooxidation of a substance B during a single potential sweep (Fig.8.4.2.) is called as current peak. As the concentration of B at the electrode-solution interface decreases monotonically, the faradaic current due to the electroreduction or electrooxidation of B increases monotonically, with time. The maximum current value is attained when the transport rate of B the electrode-solution interface is smaller than the rate at which it is removed from the interface by electrolysis.Then the current decreases monotonically with time.

The term *peak current* is also used to denote the maximum value of the faradaic current attributable to the electroreduction or electrooxidation of an electroactive substance in

techniques such as ac polarography, differential pulse polarography, and derivative polarography. However, these techniques give curves that arise in ways different from that cited above, and the terms *summit*, *summit current*, and *summit potential* were therefore recommended for use in connection with such techniques (Fig. 8.4.3). See also *Current, apex*.

Current, periodic

See *Current, alternating*.

Current, regeneration

See *Current, catalytic*.

Current, residual, i_r, I_r; A

The current that flows, at any particular value of the applied potential, in the absence of the substance whose electrode behaviour is being investigated, i.e. in a blank solution (Figs. 8.4.1, 8.4.2 and 8.4.3)
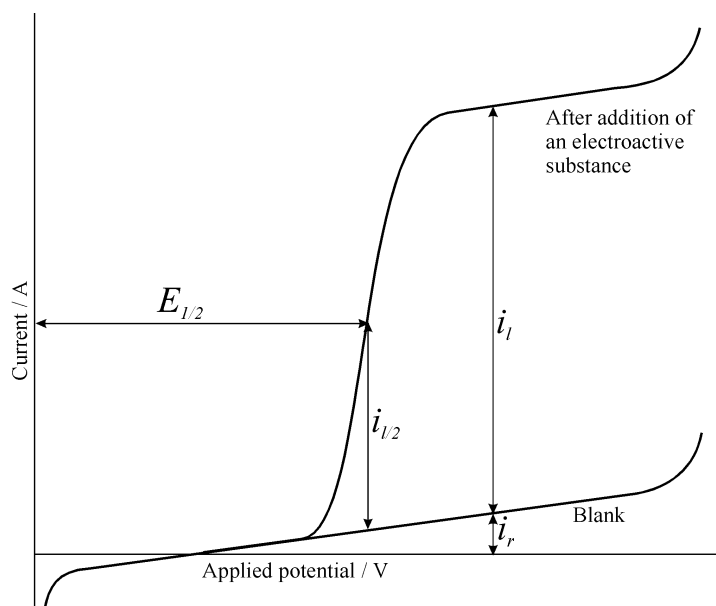

Figure 8.4.1   Idealized polarogram illustrating the limiting current, i_l, the residual current, i_r, and the half-wave potential $E_{1/2}$
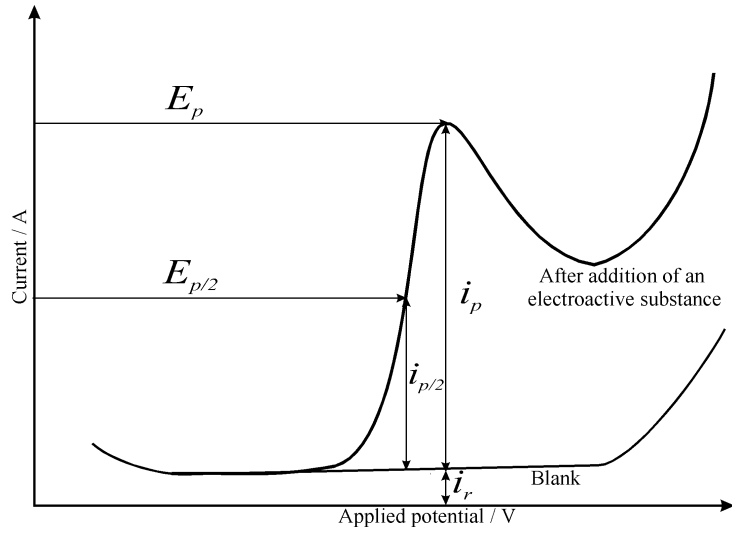
Figure 8.4.2   Idealized linear-sweep voltammogram illustrating the peak current, i_P, the residual current, i_r, the peak potential E_P, and the half-peak potential $E_{p/2}$
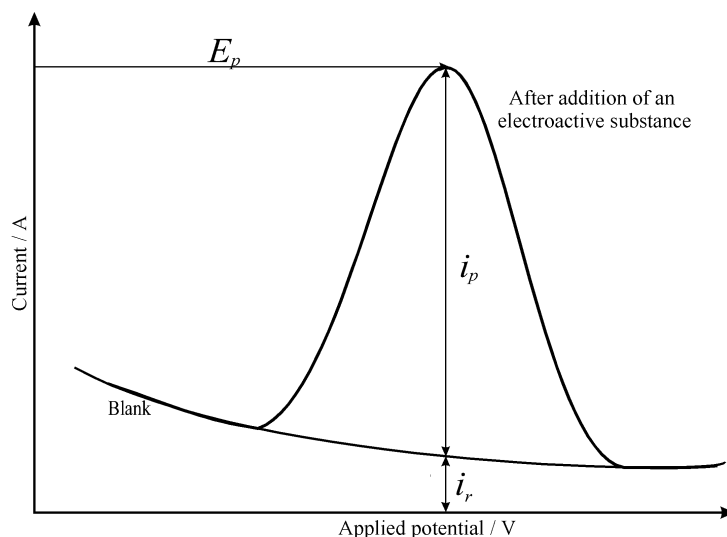
Figure 8.4.3   Idealized AC polarogram illustrating the peak current, i_p, the residual current, i_r, and the peak potential E_p

Current, square-wave, i_{sw}, I_{sw}; A

In square-wave polarography, 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).

Current, summit, i_{su}, I_{su}; A

In ac polarography, differential pulse polarography, derivative polarography, square-wave polarography, and similar techniques, the maximum value of the non-direct component of the current that is associated with the presence of a substance B. Normally, this component of the current is faradaic.   Because of the electroreduction or electrooxidation of B, its concentration decreases monotonically at the electrode-solution interface with the potential sweep rate and both direct and non-directfaradaic current components increase monotonically.When the charge transfer rate becomes larger than the diffusion rate the concebtration of B is depleted and the increase of the direct current becomes smaller. The maximum of the non-direct current arises for the largest value of the direct current change. Instead of summit current now *peak current* is preferred. See Fig.8.4.3.

Similar maxima arise if this component is non-faradaic, i.e. if B is a surface-active rather then electroactive substance. In a case known to be of the latter type, the term **apex current** is recommended as being more specific.

Depolarizer

The term *electroactive substance* should be used in preference to depolarizer.

Diffusion current constant, I ; A mol^{-1} m^3 kg$^{-2/3}$ s$^{1/2}$

In polarography, the empirical quantity defined by the equation

$$I = i_{d,l}/c_B m^{2/3} t_1^{1/6}$$

where $i_{d,l}$ is the limiting diffusion current, c_B is the bulk concentration of the substance B whose electroreduction or electrooxidation results in the recorded wave, m is the average rate of (mass) flow of mercury or other liquid metal working electrode, and t_1 is the drop time.

Drop time, t_d; s

In polarography, the time interval that elapses between the instants at which two successive drops of freely dropping liquid metal are detached from the tip of the capillary. The symbols t_1 and τ are not recommended.

Electroactive substance

In voltammetry and related techniques, a substance that undergoes a change of oxidation state, or whose chemical bonds being broken or formed, in a charge-transfer step at the working electrode.

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.

In potentiometry with ion-selective electrodes, the sensed ion plus 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.

Electrode, auxiliary

Three-electrode electrochemical cells comprise

(1)   an indicator (or test) electrode or a working electrode, at the surface of which processes of interest may occur,

(2)   a reference electrode, 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.

If processes of interest occur at both the anode and the cathode of a cell (as in differential amperometry or controlled-current potentiometric titration with two indicator electrodes), the cell should be said to comprise two indicator (or test) or working electrodes.

Electrode, counter

See *Electrode, auxiliary*.

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, with no appreciable change of bulk solution composition within the duration of a measurement.

Electrode, reference

An electrode that maintains a virtually invariant potential under the conditions prevailing in an electrochemical measurement, and that serves for observation, measurement, or control of the potential of the indicator (or test) or working electrode.

Electrode, test

See *Electrode, indicator*.

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 even sufficiently large to effect appreciable changes of bulk composition within the duration of a measurement.

Electrolyte

A solution of a dissociated salt in a solvent.

Electrolyte, base

See *Electrolyte, supporting*.

Electrolyte, indifferent

See *Electrolyte, supporting*.

Electrolyte, supporting

An electrolyte the ions of which are electroinactive in the range of applied potentials being studied, and whose ionic strength (and, therefore, contribution to the overall conductivity) is usually much larger than the concentration of an electroactive substance to be dissolved in.

Electromotive Force, E; V

Frequency; 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.

Mass-transfer-controlled electrolyte rate constant, s_B, s^{-1}

In controlled-potential coulometry and related techniques, the empirically evaluated constant of proportionality defined by the equation

$$s_B = -(1/c_B)(dc_B/dt)$$

where c_B is the bulk concentration of the substance B, and dc_B/dt is the rate of change of that concentration, resulting from the consumption of B by electroreduction or electrooxidation at the working electrode.

n, number of electrons

A stoichiometric ratio equal to the total number of electrons transferred between an electrode and a solution during electroreduction or electrooxidation 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 *Current, catalytic*).

n_{app}, number of electrons

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.

When the electroreduction or electrooxidation 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.

Outflow velocity (of mercury or other liquid metal)

See *Rate of flow*.

Peak

See *Current, peak*.

Potential, apex

See *Current, apex*.

Potential, applied, E_{app}; V

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 of resistance R, and another ohmic potential drop through each electrode. This quantity has often been denoted by the term "voltage", whose continued use is not recommended.

Potential difference, E; V

Single electrode potentials relative to hypothetical standards such as vacuum zero are not experimentally accessible. Consiquently all measured voltages are potential differences between two electrodes.

Potential, half-peak, $E_{p/2}$; V

In linear-sweep voltammetry, triangular-wave voltammetry, cyclic triangular-wave

voltammetry, and similar techniques, the potential of the working (indicator) electrode at which the difference between the total current and the residual current is equal to one-half of the peak current. This potential is attained in the interval in which the rate of the charge-transfer process, and hence the (absolute value of the) current, increases monotonically with time (Fig. 8.4.2.). The quarter-peak potential, $E_{p/4}$, the three-quarter-peak potential, $E_{p3/4}$, etc., may be similarly defined.

Potential, half-wave, $E_{1/2}$; V

The potential of a polarographic or voltammetric working (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 (Fig. 8.4.1.). The quarter-wave potential, $E_{p/4}$, the three-quarter-wave potential, $E_{p3/4}$, etc., may be similarly defined.

Potential, peak, E_P; V

In linear-sweep voltammetry, triangular-wave voltammetry, cyclic triangular-wave voltammetry, differential pulse voltammetry and similar techniques, the potential of the working (indicator) electrode at which the peak current is attained (Fig.8.4.2 and 8.4.3).

Potential, quarter-transition-time, $E_{\tau/4}$; V

In chronopotentiometry (at constant current density), 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. Appropriate correction for double-layer charging phenomena is needed in practice.

Potential, summit, E_{su}; V

In ac polarography, differential pulse polarography, derivative polarography, and similar techniques, the potential of the working (indicator) electrode at which the summit current is attained. Recently instead of summit potencial *peak potencial* is preferred (Fig. 8.4.3.).

Precursor (of an electroactive substance)

See *Electroactive substance*.

Pulse duration, t_P; s

In pulse polarography, differential pulse polarography and related techniques, the time

interval during which the excitation signal deviates from the base line. This interval includes the sampling interval.

Quantity of electricity, Q; C

The quantity of electricity that flows during the electrolysis of an electroactive substance between t_1 and t_2 is given by

$$Q = \int_{t_1}^{t_2} i_t \, dt$$

where i_t is the instantaneous current at any instant during electrolysis. The electroreduction of an electroactive substance results in negative values of Q; the electrooxidation 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 current, e.g., Q_{DL} = double-layer quantity of electricity, Q_t = instantaneous quantity of electricity, etc.

Rate of flow (of mercury or other liquid metal), average, m; kg s^{-1}

In polarography, 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_d; the average value of the instantaneous rate of flow over the entire life of the drop.

Rate of flow (of mercury or other liquid metal), instantaneous, m_t; kg s^{-1}

In polarography, the rate of increase of the mass of a drop at a particular instant $\underline{t}$ seconds after it has begun to form.

Reaction, surface

See *Current, kinetic*.

Reaction, volume

See *Current, kinetic*.

Response constant (no symbol recommended)

A quantity whose expression includes a current characteristic of a charge-transfer process and the experimental conditions under which it is investigated; the nature of the expression

depends on the technique employed. Some typical response constants are the diffusion current constant in polarography, the voltammetric constant in linear-sweep voltammetry, and the chronopotentiometric constant in chronopotentiometry.

Sampling interval

In Tast polarography, square-wave polarography, and similar techniques, the time interval during which the current is measured or recorded.

Sampling time, t_m; s

In Tast polarography, square-wave polarography, and similar techniques, the duration of the sampling interval.

Strobe interval

[In Tast polarography]. See *Sampling time*.

Tast interval

[In Tast polarography]. See *Sampling time*.

Thickness of the reaction layer, μ; m

When a kinetic current 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 at which the chemical equilibrium isestablished. 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 negligibly small.

Transition time, τ; s

In chronopotentiometry and related techniques, the time interval 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 is often taken to be the instant at which the rate of variation of the potential of the indicator electrode attains a maximum value.

Voltage, e, 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.

Voltage, alternating, e_{ac}, V

This term should be applied only to sinusoidal signal excitation; the term *periodic voltage* should be used for other wave forms.

Voltage, alternating, amplitude, e_{ac}, V

This term should denote half of the peak-to-peak distance. Peak-to-peak and **r.m.s.** amplitudes should be so specified.

Voltage, periodic, e_{pc}; V

This general term applies to square, triangular, and other wave forms; the term "alternating voltage" should be reserved for sinusoidal wave forms.

Voltammetric constant, v; A mol^{-1} V$^{-1/2}$ m s$^{1/2}$

In linear-sweep voltammetry and related techniques, the empirical quantity defined by the equation

$$v = i_p/A\ v^{1/2}\ c_B\ (\ = j_p/v^{1/2}\ c_B)$$

where i_p is the peak current, A is the area of the electrode-solution interface, v is the rate of change of applied potential, and c_B is the bulk concentration of the substance B whose reduction or oxidation is responsible for the peak in question.

Wave height

The limiting current of an individual wave, frequently expressed in arbitrary units for convenience.