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INTERNATIONAL UNION OF
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ANALYTICAL CHEMISTRY DIVISION

COMMISSION ON ELECTROANALYTICAL CHEMISTRY

RECOMMENDATIONS FOR SIGN CONVENTIONS AND PLOTTING OF ELECTROCHEMICAL DATA

(RULES APPROVED 1975)

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ANALYTICAL CHEMISTRY DIVISION
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The Commission on Electroanalytical Chemistry of the International Union of Pure and Applied Chemistry wishes to alert authors to an impending agreement on a sign convention for currents, which is at variance with prevailing practice in the electroanalytical literature. For the sake of uniformity, we urge electroanalytical chemists to use this IUPAC sign convention, which is outlined below.

The fundamental convention will consist of assigning positive values to anodic currents and negative ones to cathodic currents. Anodic and cathodic currents will continue to be defined as corresponding to net oxidation and net reduction, respectively, at the indicator or working electrode.

Conformity to this convention will require many chemists who work with polarographic waves, chronopotentiograms, and other electrochemical response curves to reformulate some of the equations associated with them and adjust related procedures.

Any reasonable choice of coordinates is appropriate in plotting any such curve, provided that the abscissa and ordinate axes are clearly labelled. Most of the polarographic and other voltammetric curves in the existing literature are plotted with cathodic currents above the abscissa axis and negative values of the applied e.m.f. to the right of the ordinate axis. Those who wish to follow the new convention and also to facilitate comparison of their curves with those in the prior literature may achieve both aims by choosing $-i$‡ as the positive ordinate and $-E$ as the positive abscissa.

Some relationships and plots will be unaltered by adoption of the new convention. An example is the analysis of a polarographic wave obtained for a Nernstian ('reversible') diffusion-controlled half-reaction of the type

$$M^{n+} + ne + Hg = M(Hg).$$

Obviously, a line having a slope of 2·3 RT/nF volt for the cathodic process will still be obtained if $-E$ is plotted against $\log_{10}[i/(i_{d,c} - i)]$, because the argument of the logarithmic term will still be positive at every point even though i (the cathodic current at the potential E) and $i_{d,c}$ (the cathodic diffusion current) are both regarded as negative. The corresponding plot for a composite anodic–cathodic wave would be one of $-E$ against $\log_{10}[(i - i_{d,a})/(i_{d,c} - i)]$, where $i_{d,a}$ is the anodic diffusion current, now regarded as positive, and this again conforms to current practice. It may be stressed that the familiar form is retained because the new convention alters the signs of both $(i - i_{d,a})$ and $(i_{d,c} - i)$.

Such cancellation of sign occurs only when the ratio of two currents is involved, and expressions that involve only a single current will require readjustment. For instance, the equation of a Nernstian ('reversible') polarographic wave corresponding to the process

$$M^{n+} + ne = M(\text{insoluble})$$

of which one common form is

$$E = \text{constant} + \frac{RT}{nF} \ln (i_{d,c} - i)$$

will have to be rewritten as

$$E = \text{constant} + \frac{RT}{nF} \ln (i - i_{d,c})$$

to avoid assigning negative values to the argument of the logarithmic term. The cathodic current i has generally been related to the difference between the concentration c of an electroreducible substance in the bulk of a solution and its concentration c° at the surface of the indicator electrode by equations of the forms

$$i = k(c - c^\circ) \quad \text{and} \quad i = nFAk_{red}c^\circ$$

for diffusion- and rate-controlled processes, respectively, and these will have to be rewritten as

$$i = -k(c - c^\circ) \quad \text{and} \quad i = -nFAk_{red}c^\circ$$

so that the cathodic current will always have the prescribed negative sign.

Other electrochemical equations should be modified, by introducing or removing a minus sign, in the fashion illustrated by the last two examples. For instance, the Ilkovič and Sand equations should be written as

$$i_d = -knD^{1/2}cm^{2/3}\tau^{1/6}$$

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‡The symbol I for electric current is recommended by IUPAC and other international organizations. However, the symbol i, generally used in the electroanalytical literature, is acceptable.

and

$$i = -\pi^{1/2} nFAD^{1/2} c/2\tau^{1/2}.$$

Polarographic diffusion current constants, chronopotentiometric constants, and similar quantities should continue to have the same signs as the currents to which they pertain, and should accordingly be taken as negative for cathodic processes.

It is strongly urged that due consideration be given to all relevant IUPAC conventions and to problems of internal consistency in using all equations or definitions likely to be affected by the new convention, and in specifying the sign of any quantity appearing in those equations.