Planar diffusion to macro disc electrodes - What electrode size is required for the Cottrell and Randles-Sevcik equations to apply quantitatively?[†]

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Abstract

Simulations and experiments are reported which investigate the size of a macro disc electrode necessary to *quantitatively* show the chronoamperometric or voltammetric behaviour predicted by the Cottrell equation or the Randles-Sevcik equation on the basis of exclusive one-dimensional diffusional mass transport. For experimental time scales of several seconds, the contribution of radial diffusion is seen to be measurable even for electrodes of millimetres in radius. Recommendations on the size of macro electrodes for quantitative study are given and should exceed 4 mm radius in aqueous solution.

Introduction

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The use of microelectrodes for the best-practice measurement of electrochemically derived data, such as heterogeneous rate constants, diffusion coefficients, fast coupled homogeneous reaction kinetics and analytical considerations, is well-established. This approach is largely based on the pioneering work of Amatore [1, 2] and was further implemented by Bond [3, 4] and others [5, 6]. Recently – and partly driven by the need to interrogate the diverse, complex and ever increasingly imaginative methods for possible energy conversion and storage as well as for analysis – there has been a renaissance in macro electrode measurements both employing rotating disc electrodes [7, 8], but also, and especially, cyclic voltammetry using macro electrodes [9], as originally introduced by the classical work of Nicholson and Shain [10, 11].

The simplicity of using macro electrodes, other than the practical ease of size, lies in the assumption that diffusional transport to the electrode surface will be planar and one-dimensional. Thus, and usually in contrast to microelectrodes, theoretical equations can often be derived in mathematically analytical forms for the purpose of comparison with experiments. Thus, the current-time (*I*-*t*) response resulting from a potential step from zero current to diffusion-limited conditions applied to the sample redox process:

$$A \pm e^- \leftrightarrows B$$

is given by the Cottrell equation known to all electrochemists [12]:

$$I = \frac{\mathrm{F}A\sqrt{D}}{\sqrt{\pi t}}[A]_{\mathrm{bulk}} \qquad (1)$$

where D is the diffusion coefficient, $[A]_{\mathrm{bulk}}$ the bulk concentration of species A in the solution, F is the Faraday constant and A the electrode area (for a disc of radius r_e the area $A = \pi r_e^2$).

Similarly, assuming that the redox couple A/B is electrochemically reversible under the prevailing mass transport conditions, the peak current I_P for cyclic voltammetry is predicted to be:

$$I_P = \ 0.446\ \mathrm{F}\ \pi r_e^2 \sqrt{\frac{\mathrm{F}D\nu}{\mathrm{R}T}}\ [A]_{\mathrm{bulk}} \qquad (2)$$

where v is the scan rate, T is the temperature and R the universal gas constant[13]. Both equations (1) and (2) result from solving Fick's laws of diffusion [14, 15] in one spatial dimension with the appropriate boundary conditions.

Given the renaissance of macro electrode measurements, it is interesting to consider under which conditions equations (1) and (2) can be applied *quantitatively*, not least since it has recently been asserted

that macro electrode experiments may lead to a great diversity of results when applied to the same system, but by different groups [16–18]. Moreover, this variation has been such as to apparently stimulate the introduction of elaborate new techniques such as FFT (Fast Fourier Transformation) voltammetry in an attempt to improve the reproducibility [19, 20].

Among the primary features for the applicability of equation (1) and (2) are the need for tight thermostating, application of the appropriate potential range such that the voltage seen is not reversed prematurely relative to a cyclic voltammetry peak [13], the avoidance of using second or later scan data, the avoidance of natural convection [21, 22] the recognition that the use of a digital potentiostat can broaden voltammetric measurements [23] and the need to ensure that the electrode is flat and neither rough nor porous [24, 25]. However, one further very simple consideration has to be addressed, namely how large does the electrode have to be in order to quantitatively comply with equations (1) and (2)? In other words what is the contribution of radial diffusion (often referred to as 'edge effect') to chronoamperometry and cyclic voltammetry carried out at macro electrodes? Answering these questions is the aim of this present note and will be approached from both simulation and experimental perspectives.

Experimental

Chemicals and electrochemical setup

The electrolyte used was an aqueous solution of 9.50 mM of potassium ferrocyanide $K_4[Fe(CN)_6]$ (Lancaster, UK) and 0.50 M potassium nitrate KNO_3 (BDH). This solution was prepared by dissolving the respective analytical grade chemicals in high-purity water (Millipore, resistivity not less than 18.2 MΩcm at 25 °C).

Electrochemical measurements were performed using a three electrode setup comprising a carbon rod counter electrode, a saturated calomel reference electrode (SCE, $E = 0.241$ V vs standard hydrogen electrode, BASi Inc.) and either one of two differently sized glassy carbon working electrodes (BASi Inc.). The two working electrodes were sized to 1.49±0.02 mm and 0.78±0.03 mm in radius using optical microscopy (Unicam Instruments LTD). The working electrodes were first polished to a mirror surface using diamond spray (Kemet, particle size 1.0 μm and 0.3 μm) and then sonicated in high-purity water for 1 minute prior to each measurement. During electrochemical measurements tight thermostating of the entire electrochemical cell to under ±0.2 °C was ensured by placing the cell in a thermostated water bath

inside a thermostated Faraday cage. All measurements were performed in stagnant solutions using a µAutolab III (Metrohm) potentiostat.

Diffusion coefficient measurements

Temperature-dependent diffusion coefficients of $[Fe(CN)_6]^{4-}$ in the used electrolyte were determined by steady-state voltammetry at a platinum micro disc working electrode (radius = 4.8 µm, calibrated using ruthenium hexa-amine) in the temperature range from 24.0 °C to 28.0°C. The potential was scanned from -0.15 V to 0.6 V vs SCE at a scan rate of 25 mVs^{-1}.

Chronoamperometry

To quantify the effect of radial diffusion on chronoamperometry at conventional commercial 'macro' electrodes the oxidation of ferrocyanide at two differently sized glassy carbon electrodes was studied under mass transport limited conditions. For this purpose, the applied potential was changed from -0.2 V vs SCE to 0.35 V vs. SCE in a single step and the resulting current was recorded for 10 seconds. For each electrode size three separate chronoamperometric experiments were performed. Blank measurements were acquired in a solution of 0.50 M KNO_3 and were subtracted from the chronoamperograms obtained in the presence of ferrocyanide to remove capacitive contributions from the Faradaic signal.

Convection of the electrolyte was kept at an experimental minimum by avoiding temperature gradients and mechanical perturbation of the electrolyte as well as by restricting the experimental time scale to short durations (10 s) in order to avoid natural convection.

Simulation

A simulation for a cyclic voltammetry measurement was carried out for an ideal reduction/oxidation system containing a disc electrode with varied radius. In the model the transport of the electrochemical species in solution is described for fully supported electrolyte conditions. The thus obtained diffusion controlled system was solved numerically using Fick's second law in a two-dimensional cylindrical space [26]:

$$\frac{\partial[A]}{\partial t} = D\left(\frac{\partial^2[A]}{\partial r^2} + \frac{1}{r}\frac{\partial[A]}{\partial r} + \frac{\partial^2[A]}{\partial z^2}\right) \quad (3)$$

for a representative D of 10^{-9} m^2s^{-1} and an initial concentration of [A] = 1 mM. A reversible boundary condition was applied on the disc electrode surface to relate the potential V to the surface concentrations of the oxidant c_{ox} and the reductant c_{red} were described by the Nernst expression:

$$\left(V - E_f^{\ominus}\right)\frac{F}{RT} = \ln\left(\frac{c_{ox}}{c_{red}}\right) \quad (4)$$

$E_f^{\ominus}$ is the formal potential. Insulation boundary conditions are used for the cell walls and axial symmetry condition at $r = 0$. We also simulated a 'macro' case of an infinite disc radius using a one dimensional system. In this case the Fick's second law follows:

$$\frac{\partial[A]}{\partial t} = D\left(\frac{\partial^2[A]}{\partial x^2}\right) \quad (5)$$

The simulations of the cyclic voltammetry were made using a finite difference approach based on the Alternating Direction Implicit (ADI) method as detailed fully in ref [27]. The simulations were coded in C++ with the Open Multi-Processing (OpenMP) library for parallel computing. The grid distances and the time step were studied and chosen to be sufficiently small to get an accurate calculation and full numerical convergence. All simulations were carried out on an Intel® 3.2 GHz computer with 2.5 GB RAM and computing times of up to 240 minutes per cyclic-voltammetry simulation were required in order to obtain a highly accurate two dimensional simulation.

Results and Discussion

First, finite potential step chronoamperometry is considered using the ferrocyanide/ferricyanide ($[Fe(CN)_6]^{4-}$ / $[Fe(CN)_6]^{3-}$) redox couple as a model. Experiments were performed at glassy carbon electrodes of radii of 1.49±0.02 mm and 0.78±0.03 mm employing an aqueous solution of 9.50 mM $K_4[Fe(CN)_6]$ and 0.50 M KNO_3 as the electrolyte. Figure 1 shows the current-time transients resulting from a potential step from -0.2 V vs SCE to +0.35 V vs SCE, corresponding to a potential of zero current to mass transport limited oxidation of ferrocyanide.

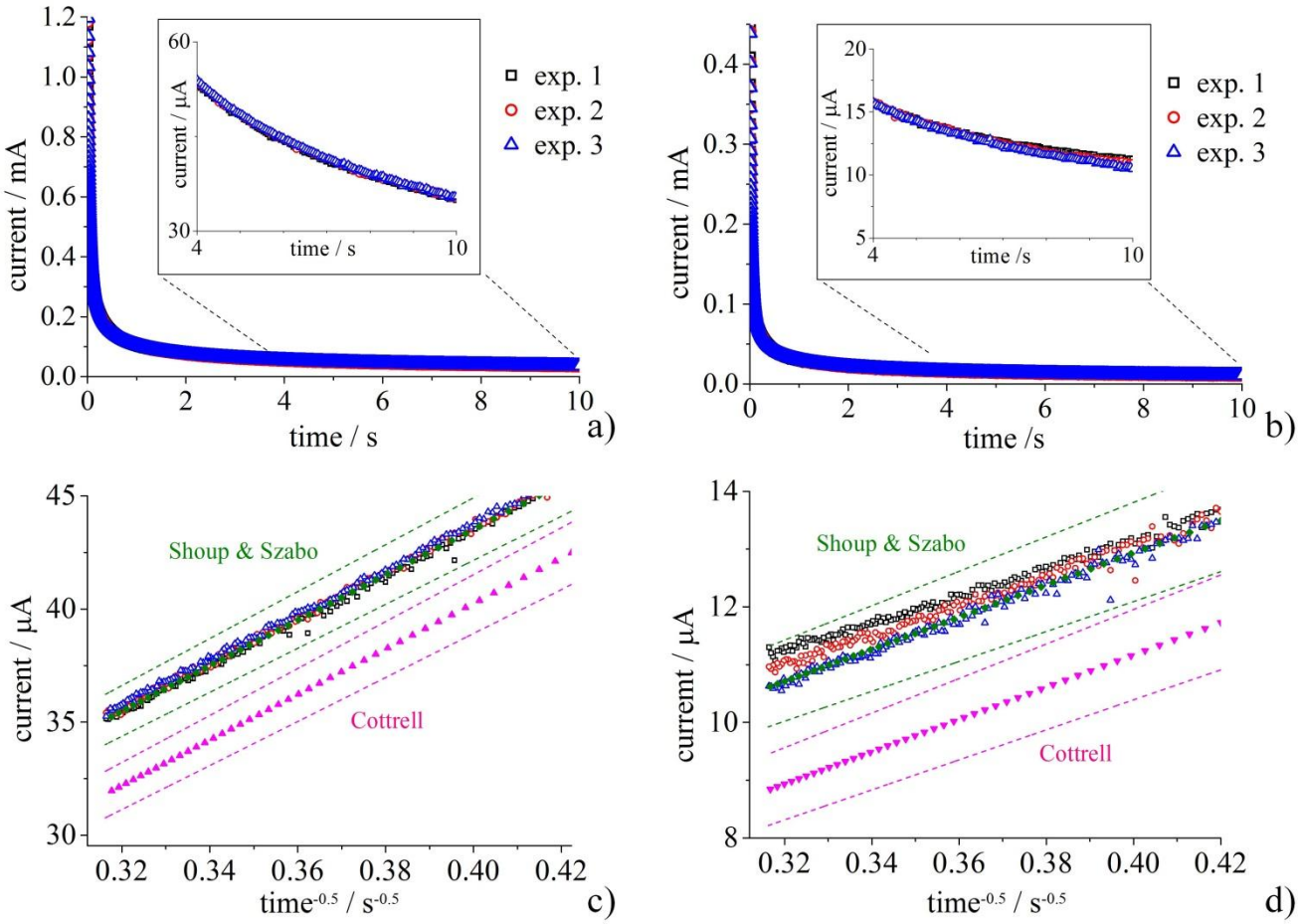

Figure 1: Experimental chronoamperograms (*I*-*t*) recorded for 3 experiments (empty symbols) during the mass transport limited oxidation of $Fe(CN)_6]^{4-}$ at millimeter-sized glassy carbon electrodes of a) r_e = 1.49 mm and b) r_e = 0.79 mm and c,d) the comparison of experimental currents (empty symbols) with theoretical currents (solid symbols) as predicted by the Cottrell equation (eq. (1), pink) and the Shoup and Szabo equations (eq. (7)-(9), green); the dashed lines show the respective theoretical currents for maximum experimental variations according to the estimated errors in *D* and r_e; electrolyte: 9.50 mM $K_4Fe(CN)_6$, 0.5 M KNO_3, potentiostated at *E* = 0.35 V vs SCE, time step for current measurement: 0.001 s, temperature = 26.0±0.2 °C.

In order to fit the experimental data to the Cottrell equation (equation 1), it is necessary to know the electrode size and the diffusion coefficient of $Fe(CN)_6]^{4-}$ in the electrolyte at the experimental temperature. The former was measured (see Experimental) by optical microscopy to 1.49±0.02 mm and 0.78±0.03 mm radius for the two electrodes. The diffusion coefficient of $Fe(CN)_6]^{4-}$ was measured using a platinum micro electrode (radius r_e = 4.8 µm) and calculated from the resulting limiting current according to:

$$I_{ss} = 4\mathrm{F}r_e D[A]_{bulk} \qquad (6)$$

for different temperatures in the range of 24 °C to 28 °C. The measured steady-state voltammograms and the Arrhenius diagram derived from this data are plotted in Figs. 2a and 2b. Thus, the diffusion coefficient of $Fe(CN)_6]^{4-}$ at the used experimental conditions and the error associated with the estimated maximum temperature uncertainties during the chronoamperometric analysis were determined. Note that the obtained value for *D* at 25 °C is in agreement with the values reported for similar electrolytes [28] and the temperature dependency yields an activation energy E_a for diffusion of ca. 15.7±0.3 kJ mol^{-1} ‡, a value close to that expected from the temperature-dependent viscosity of water [29]. Based on this, the value of *D* for the experimental temperature of 26 °C for all chronoamperometric measurements was determined to be 7.68±0.03×10^{-10} m^{2}s^{-2} (estimating an experimental temperature error of ±0.2 °C).

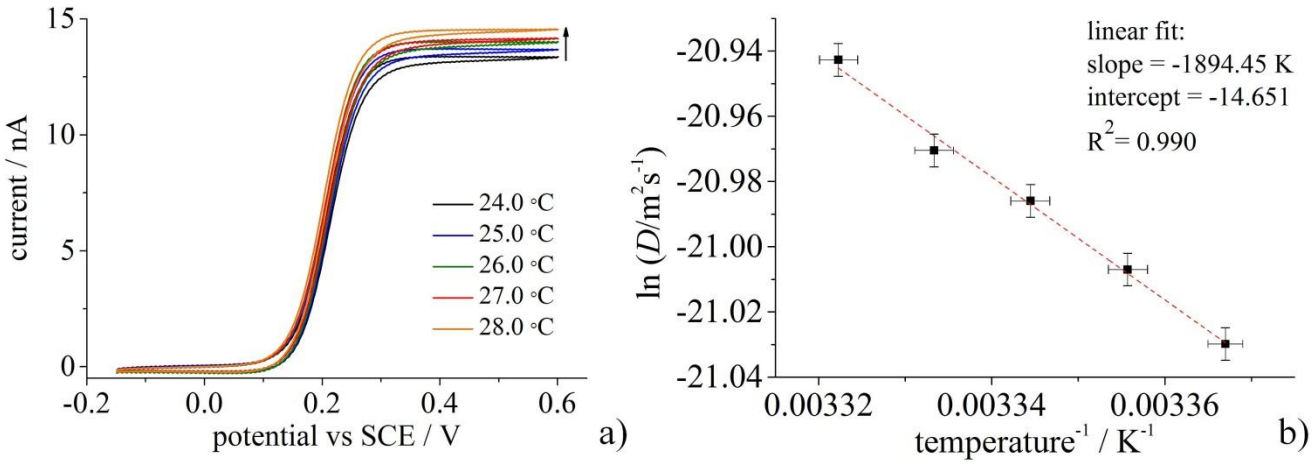

Figure 2: a) Steady-state voltammograms at a Pt micro disc electrode (r_e = 4.8 µm) recorded at different temperatures. b) Arrhenius plot (ln *D* vs. T^{-1}) of the derived diffusion coefficient of $Fe(CN)_6]^{4-}$ as a function of temperature; the linear fit (dashed line) of the data and the fitted parameters are given in the figure.

The values for the *Cottrellian* current (according to eq. (1), pink triangles) shown in Fig 1c and 1d and the expected error calculated from the possible uncertainties in the electrode size and diffusion coefficient (pink dashed lines) reveal that over the time scale from 0 to 10 seconds the experimental currents are clearly larger than predicted. The difference between the predicted and the observed current is greater for the smaller electrode (Fig. 1d) than for the larger one (Fig. 1c). Natural convection is not thought to play a dominant role at the timescale of interest (≤10 seconds), so the additional contribution of radial diffusion was considered as a plausible explanation for the augmented currents observed. Potential step chronoamperometry under these conditions has been extensively simulated and a particularly reliable calculation was reported by Shoup and Szabo [30]. The accuracy of their approach has been confirmed by

‡ The Arrhenius relation is ln *D* = constant - $E_a R^{-1} T^{-1}$, hence, the slope of the linear fit shown in Fig. 2b provides the activation energy for the diffusion of $Fe(CN)_6]^{4-}$ in the electrolyte upon multiplication by -R.

many works[31–34]. For instance Klymenko, Svir et al. [35] presented their simulations on the basis of the *Shoup and Szabo* equations, which have been found well-suited for the analysis of experimental data [36, 37].

$$I = 4\mathrm{F}Dr_{\mathrm{e}}[A]_{\mathrm{bulk}}\,\mathrm{f}(\tau) \quad (7)$$

where the dimensionless time τ is defined as

$$\tau = 4Dtr_{\mathrm{e}}^{-2} \quad (8)$$

For short dimensionless times ($\tau < 1$) f(τ) can be approximated as

$$\mathrm{f}(\tau) = \left(\frac{\pi}{4\tau}\right)^{0.5} + \frac{\pi}{4} + 0.094\tau^{0.5} \quad (9)$$

and for long times ($\tau > 1$)

$$\mathrm{f}(\tau) = 1 + 0.71835\tau^{-0.5} + 0.05626\tau^{-1.5} - 0.00646\tau^{-2.5} \quad (10)$$

The use of equations (7-9) to appropriately model the data presented in Fig. 1a and 1b suggests that the observed deviation from the purely Cottrellian behaviour can be attributed to radial diffusion effects. Figure 1c and 1d show the excellent agreement between experiment and theory, validating that diffusion-only mass transport conditions were achieved in the experiment. It follows that electrodes of 0.78 mm and 1.49 mm radius are *not* sufficiently large to ensure pure one-dimensional diffusion over a time scale of several seconds. Note that such electrode dimensions are typical sizes of many commercially supplied 'macro' electrodes.

Given the significant contribution of radial diffusion to chronoamperometric currents at millimetre-sized electrodes, the effect of these contributions on cyclic voltammetry will be considered and quantified using simulations in the following section.

For this purpose the above-mentioned A/B redox couple was assumed to be fully electrochemically reversible and Nernst boundary conditions were applied to predict the current. Voltammetric curves in the presence and absence of radial diffusion were simulated and validated by comparison with analytical theory [27]. Figure 3 depicts the simulated voltammograms.

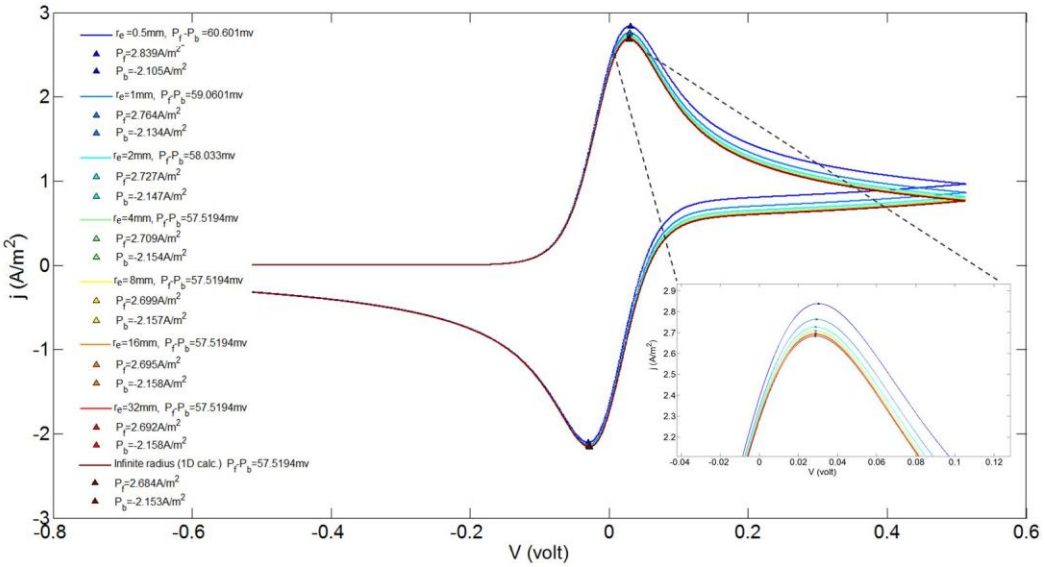

Figure 3: Voltammograms simulated assuming an electrochemically reversible redox couple A/B with Nernst boundary conditions and diffusion coefficients of $D_A = D_B = 1\times10^{-9}$ m^2s^{-2}. Voltammetric currents for various electrode sizes (radius = r_e) are normalized by the area ($A = \pi r_e^2$ of the macro disc working electrode and the resulting current densities (j) are shown. The inlay provides an enlarged view of the oxidative forward peak (P_f) current densities (j_P).

A visible – and experimentally measureable – difference between the behaviour calculated using planar diffusion only and the full simulation of the finite electrode size is apparent. The 'reversibility' of redox couples is generally measured via the peak-to-peak voltage separation E_{pp}. Table 1 summarises the variations of the peak current density j_P and E_{pp} values for different electrode sizes and scan rates, taking all other parameters as given in Figure 3. It is again evident that the electrodes of size of ca. 1 mm radius show significant deviations from the simple one-dimensional diffusion limit. Note that experimental observations of this kind in experiments could easily be miss-interpreted as electrode kinetics rather than geometric, mass transport effects.

Table 1: Simulated voltammetric peak to peak separations and oxidative peak current densities for 'macro' disc electrodes of different radii in comparison to the results expected for a truly one-dimensional planar diffusion to an electrode of infinite size.

electrode radius r_e / mm	Peak-to-peak separation E_{PP} / mV	ox. peak current density j_P / Am^{-2}
0.5	60.60	2.84
1	59.06	2.76
2	58.0	2.73
4	57.52	2.71
8	57.52	2.70
16	57.52	2.69
32	57.52	2.69
infinite (1D calc.)	57.52	2.68

Conclusions

If quantitative measurements are to be made in which experiments are coupled with theory then macro electrodes need to be selected with multi-millimeter radius to avoid contributions of 'edge effects' originating from radial contributions. Several commercially available 'macro' electrodes are likely to be too small to meet this requirement; rather electrodes of size not less than 4 mm radius are recommended for investigations in aqueous solutions. As diffusion coefficients of redox species are typically larger in organic solvents and smaller in many room temperature ionic liquids, larger and smaller minimum electrode sizes are required for a true 'macro' response in these cases, respectively. Alternatively, the use of microelectrodes may be preferred, especially for electro kinetic measurements.

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