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A family of approximations for the numerical computation of the Randles–Sevcik function in electrochemistry

Frank G. Lether

Mathematics Department, Boyd Graduate Research Center, University of Georgia, Athens, GA 30602-7403, USA
E-mail: fglether@math.uga.edu

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Dedicated to the 80th birthday of Professor Frank Harary

An integral representation for the reversible Randles–Sevcik function is developed using some relations from the theory of special functions. This integral formulation is employed to generate a two-parameter family of analytical expressions for computing the reversible Randles–Sevcik function correct to a specified number of decimal digits. This work extends the practical application of a novel series expression for the Randles–Sevcik function previously developed by Oldham.

KEY WORDS: Randles–Sevcik function, series expression, two-parameter

1. Introduction

The reversible Randles–Sevcik function $\pi^{1/2}\chi(x)$ arises in electrochemistry, where it characterizes the dependence of electric current on cell voltage under certain electrolysis conditions [1–3]. As illustrated by the table in Oldham [4] and the plot in [5], the graph of $\pi^{1/2}\chi(x)$ over $-\infty < x < \infty$ is a positive, asymmetrical curve with a single, relatively steep peak near $x = 1.1$. For positive and negative values of x, the Randles–Sevcik function exhibits the notably different asymptotic properties specified by $\pi^{1/2}\chi(x) \sim (\pi x)^{-1/2},\ x \to \infty$, and $\pi^{1/2}\chi(x) \sim \mathrm{e}^x,\ x \to -\infty$. Furthermore, poles of the Randles–Sevcik in the complex plane restrict the convergence of its Maclaurin series to the finite interval $-\pi < x < \pi$. The combination of all of these factors make it difficult in practice to obtain analytical expressions for $\pi^{1/2}\chi(x)$ that are valid over the complete domain $(-\infty, \infty)$ of the function.

For negative x, Reinmuth [6] showed that the Randles–Sevcik function can be expressed as the convergent series

$$\pi^{1/2}\chi(x) = \sum_{n=1}^{\infty}(-1)^{n+1}n^{1/2}\mathrm{e}^{nx}, \quad x < 0. \tag{1.1}$$

For negative x bounded away from zero, the partial sums of (1.1) provide an effective way to compute the Randles–Sevcik function. However, this latter interval does not include the chemically interesting region containing the peak of $\pi^{1/2}\chi(x)$.

In an effort to overcome these problems, Oldham [4,7] used the fractional calculus to show that the Randles–Sevcik function can be expressed as the Weyl semiderivative of the function $g(x) = 1/(1+\mathrm{e}^{-x}) = 1/2 + 1/2\tanh(x/2)$:

$$\pi^{1/2}\chi(x) = \frac{\mathrm{d}^{1/2}g(x)}{\mathrm{d}x^{1/2}} = \frac{\mathrm{d}}{\mathrm{d}x}\left(\frac{\mathrm{d}^{-1/2}g(x)}{\mathrm{d}x^{1/2}}\right) = \frac{\mathrm{d}}{\mathrm{d}x}\left(\pi^{-1/2}\int_{-\infty}^{x}(x-y)^{-1/2}g(y)\,\mathrm{d}y\right).$$

Using this approach and the partial fraction representation for $g(x)$, Oldham was able to analytically continue the Reinmuth series representation (1.1) to the whole domain of the Randles–Sevcik function through the novel series reformulation

$$\pi^{1/2}\chi(x) = \left(\frac{\pi}{2}\right)^{1/2}\sum_{n=1}^{\infty}\gamma_n(x), \tag{1.2}$$

where $\gamma_n(x) = \beta_n^{-3}(\beta_n - x)^{1/2}(\beta_n + 2x)$, $\beta_n = (x^2 + b_n^2)^{1/2}$, $b_n = (2n-1)\pi$. In practice the convergence of Oldham's series (1.2) is unacceptably slow. For example, if $x = 0$ and we require an absolute error less than 0.001, then we must sum about $N = 50{,}660$ terms.

Oldham recognized this problem and developed a method to accelerate the rate of convergence by essentially adding and subtracting a known convergent series, whose nth term mimics the Maclaurin series behavior of $\gamma_n(x)$ in (1.2). For the specific details see [4,7] and the extensions in [5]. Although these latter accelerated series developments are of much greater practical use than (1.2) in the neighborhood of $x = 0$, their rate of convergence dramatically slows as x moves away from the origin. In view of these observations it seems worthwhile to see if a more uniform method can be developed for determining analytical approximations to $\pi^{1/2}\chi(x)$ that are of use over the whole domain $(-\infty, \infty)$ of the Randles–Sevcik function.

The main purpose of this paper is to develop a two-parameter family of analytical approximations of the form

$$\pi^{1/2}\chi(x) \approx S_N(x) + E_{N,K}(x), \quad -\infty < x < \infty, \tag{1.3}$$

where $N \geqslant 1$ and $K \geqslant 0$ are integer parameters that control the accuracy of the approximation;

$$S_N(x) = \left(\frac{\pi}{2}\right)^{1/2}\sum_{n=1}^{N}\gamma_n(x), \tag{1.4}$$

is the Nth partial sum of (1.2); $E_{N,K}(x)$ is an error correction term given by

$$E_{N,K}(x) = \sum_{k=0}^{K} d_k\left(x^2 + 4N^2\pi^2\right)^{-k-1/4}\sin\left[\left(2k+\frac{1}{2}\right)\theta_N + \frac{\pi}{4}\right], \tag{1.5}$$

Table 1
Coefficients (1.6) required for the error correction summation (1.5): $d_k = e_k \pi^{2k-1/2},\ k = 0, 1, \dots, 7.$

k	e_k	k	e_k
0	1	4	$\frac{54483}{32768}$
1	$-\frac{1}{8}$	5	$-\frac{10728445}{786432}$
2	$\frac{49}{384}$	6	$\frac{10508149633}{62914560}$
3	$-\frac{341}{1024}$	7	$-\frac{95840228925}{33554432}$

where $\theta_N = \tan^{-1}[x/(2N\pi)]$, the coefficients d_k being defined in terms of the Bernoulli numbers and the gamma function by

$$d_k = 2\bigl(1 - 2^{2k-1}\bigr) B_{2k} \pi^{2k-1} \frac{\Gamma(2k + 1/2)}{(2k)!} = e_k \pi^{2k-1/2}. \tag{1.6}$$

The first eight of these coefficients are listed in table 1.

For our introductory purposes here we merely illustrate the above results for the simplest and least accurate case corresponding to $N = 1$ and $K = 0$ in the family of approximations (1.3). In particular,

$$\pi^{1/2}\chi(x) \approx S_1(x) + E_{1,0}(x) \tag{1.7}$$

where the first partial sum of (1.2) is

$$S_1(x) = \left(\frac{\pi}{2}\right)^{1/2} \bigl(x^2 + \pi^2\bigr)^{-3/2} \Bigl(\sqrt{x^2 + \pi^2} - x\Bigr)^{1/2} \Bigl(\sqrt{x^2 + \pi^2} + 2x\Bigr)$$

and the error correction term

$$E_{1,0}(x) = \pi^{-1/2}\bigl(x^2 + 4\pi^2\bigr)^{-1/4} \sin\left[\frac{1}{2}\tan^{-1}\left(\frac{x}{2\pi}\right) + \frac{\pi}{4}\right].$$

In figure 1 we plot the error curve $\pi^{1/2}\chi(x) - [S_1(x) + E_{1,0}(x)]$ for the simple approximation (1.7).

As can be seen from this graph, the error is fairly small, even for this lowest order member of the family of approximations (1.3). As we shall demonstrate later, much more accurate approximations result if we increase the value of N and K in (1.3). For example, the magnitude of the error on $(-\infty, \infty)$ is less than $6.4 \cdot 10^{-5}$ if $N = 2$ and $K = 1$, and less than $2.5 \cdot 10^{-16}$ when $N = 8$ and $K = 7$. The error curve $\pi^{1/2}\chi(x) - [S_8(x) + E_{8,7}(x)]$ for the latter case is shown in figure 2.

As an implementation aid we will later provide a convenient contour plot for selecting values of N and K sufficient for (1.3) to achieve a specified number of decimal digits of accuracy over $(-\infty, \infty)$.

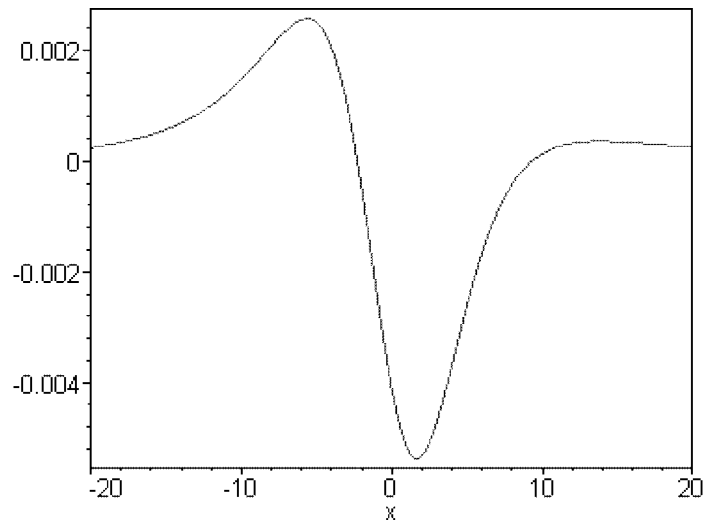

Figure 1. Error curve $\pi^{1/2}\chi(x) - [S_1(x) + E_{1,0}(x)]$ for approximation (1.3), $N = 1$, $K = 0$.

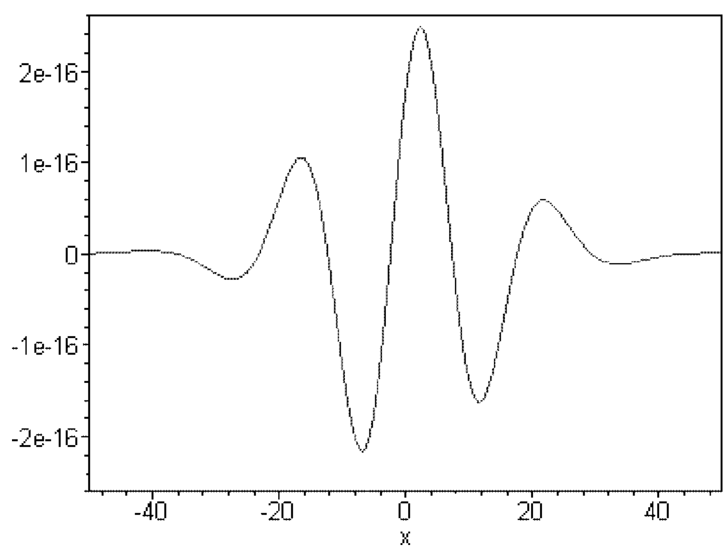

Figure 2. Error curve $\pi^{1/2}\chi(x) - [S_8(x) + E_{8,7}(x)]$ for approximation (1.3), $N = 8$, $K = 7$.

This paper is organized as follows. Sections 2 and 3 outline the mathematical derivation of the central approximation scheme specified by equations (1.3)–(1.6). Section 4 is devoted to the application of approximation (1.3) and presents a method for selecting appropriate values of N and K for computing $\pi^{1/2}\chi(x)$ to a specified number of decimal digits of accuracy. Finally, section 5 gives some concluding remarks and observations.

2. An integral form for the remainder

To develop a family of analytical approximations for the Randles–Sevcik function we employ as our principal mathematical tool the integral representation

$$\pi^{1/2}\chi(x) = \int_0^\infty t^{1/2}\,\mathrm{csch}\,\pi t\,\sin\left(xt + \frac{\pi}{4}\right)\mathrm{d}t, \tag{2.1}$$

whose technical derivation is outlined in the appendix to this paper. Equation (2.1) is the basis for all of the following analytical work.

We begin with the hyperbolic cosecant identity

$$\mathrm{csch}\,\pi t = 2\sum_{k=1}^{N} \mathrm{e}^{-(2k-1)\pi t} + \mathrm{e}^{-2N\pi t}\,\mathrm{csch}\,\pi t \tag{2.2}$$

that derives from the geometric series with remainder term, generated from the defining exponential form of $\mathrm{csch}\,\pi t$. Substituting the right-hand side of (2.2) into equation (2.1), we find with the aid of a table of Fourier-sine and cosine transforms [9] that

$$\pi^{1/2}\chi(x) = \pi^{1/2}\sum_{n=1}^{N}\left(x^2 + b_n\right)^{-3/4}\sin\left(\frac{3}{2}\alpha_n + \frac{\pi}{4}\right) + R_N(x), \tag{2.3}$$

where the angle $\alpha_n = \tan^{-1}(x/b_n)$ and the remainder

$$R_N(x) = \int_0^\infty t^{1/2}\mathrm{e}^{-2N\pi t}\,\mathrm{csch}\,\pi t\,\sin\left(xt + \frac{\pi}{4}\right)\mathrm{d}t. \tag{2.4}$$

A straight-forward, but tedious calculation shows that the summation in (2.3) is equal to the Oldham partial sum $S_N(x)$ defined by (1.4), and, consequently, that

$$\pi^{1/2}\chi(x) = S_N(x) + R_N(x). \tag{2.5}$$

Equation (2.5) shows that if we only sum the first N terms in Oldham's series (1.2), then we commit a truncation error whose magnitude is $|R_N(x)|$. Using (2.4), (2.5) and the basic inequality $\mathrm{csch}\,\pi t < (\pi t)^{-1}$ we obtain the uniform upper bound

$$\begin{aligned}\left|\pi^{1/2}\chi(x) - S_N(x)\right| = \left|R_N(x)\right| &\leqslant \int_0^\infty t^{-1/2}\mathrm{e}^{-2N\pi t}\,\mathrm{d}t \\ &= \pi^{-1}(2N)^{-1/2}, \quad -\infty < x < \infty.\end{aligned}$$

This upper bound explicitly shows that the partial sums of (1.2) do not by themselves provide a practical method for computing the Randles–Sevcik function, since to guarantee an absolute error $\varepsilon \ll 1$, we must choose $N \geqslant 2^{-1}\pi^{-2}\varepsilon^{-2} \gg 1$, e.g., for $\varepsilon = 0.001$ this gives $N \geqslant 50{,}661$.

The central idea in deriving a practical approximation to the Randles–Sevcik function from the decomposition (2.5) depends on the fact that we can accurately estimate the integral in equation (2.4) for the remainder $R_N(x)$. This is done in the next section and is the key to obtaining the family of approximations (1.3).

3. Estimating the remainder

To estimate the remainder $R_N(x)$ in (2.5) we first observe that the integrand in (2.4) is bounded in magnitude by the function

$$f_N(t) = \sqrt{t}\mathrm{e}^{-2N\pi t}\operatorname{csch}\pi t = 2\sqrt{t}\mathrm{e}^{-(2N+1)\pi t}\left[1 + \frac{\mathrm{e}^{-2\pi t}}{1-\mathrm{e}^{-2\pi t}}\right] \approx 2\sqrt{t}\mathrm{e}^{-(2N+1)\pi t}$$

with $f_N(t) \to \infty$ as $t \to 0^+$ and $f_N(1) \approx 2\mathrm{e}^{-(2N+1)\pi}$. In particular, $f_1(1) \approx 0.16 \cdot 10^{-3}$, $f_2(1) \approx 0.30 \cdot 10^{-6}$ and $f_3(1) \approx 0.56 \cdot 10^{-9}$. Consequently, as N increases the major contributing portion of the integrand in (2.4) occurs on the interval $0 < t < 1$. On this latter interval it is known that the hyperbolic cosecant admits a series expansion [8] that we express in the form

$$\operatorname{csch}\pi t = C_K(t) + \sum_{k=K+1}^{\infty} a_k\pi^{2k-1}t^{2k-1}, \quad 0 < |t| < 1, \tag{3.1}$$

where the integer $K \geqslant 0$,

$$a_k = 2\left(1 - 2^{2k-1}\right)\frac{B_{2k}}{(2k)!}$$

and the partial sum

$$C_K(t) = \sum_{k=0}^{K} a_k\pi^{2k-1}t^{2k-1} = \frac{1}{\pi t} - \frac{1}{6}\pi t + \frac{7}{360}\pi^3t^3 - \cdots + a_K\pi^{2K-1}t^{2K-1}. \tag{3.2}$$

Substituting (3.1) into (2.4) yields the identity

$$R_N(x) = E_{N,K}(x) + \delta_{N,k}(x), \tag{3.3}$$

or in view of (2.5), the representation

$$\pi^{1/2}\chi(x) = S_N(x) + E_{N,K}(x) + \delta_{N,K}(x), \tag{3.4}$$

where

$$\delta_{N,K}(x) = \int_0^{\infty} t^{1/2}\mathrm{e}^{-2N\pi t}\left[\operatorname{csch}\pi t - C_K(t)\right]\sin\left(xt + \frac{\pi}{4}\right)\mathrm{d}t, \tag{3.5}$$

$$\begin{aligned} E_{N,K}(x) &= \int_0^{\infty} t^{1/2}\mathrm{e}^{-2N\pi t}C_K(t)\sin\left(\pi t + \frac{\pi}{4}\right)\mathrm{d}t \\ &= \sum_{n=0}^{K} a_k\pi^{2k-1}\int_0^{\infty} t^{2k-1/2}\mathrm{e}^{-2N\pi t}\sin\left(xt + \frac{\pi}{4}\right)\mathrm{d}t. \end{aligned} \tag{3.6}$$

Using [9] we find that

$$\int_0^{\infty} t^{2k-1/2}\mathrm{e}^{-2N\pi t}\sin\left(xt + \frac{\pi}{4}\right)\mathrm{d}t = \frac{\Gamma(2k+1/2)}{(x^2+4N^2\pi^2)^{k+1/4}}\sin\left[\left(2k + \frac{1}{2}\right)\theta_N + \frac{\pi}{4}\right],$$

where as in section 1, $\theta_N = \tan^{-1}[x/(2N\pi)]$. If this latter integral is substituted into (3.6) we obtain the form for the error correction term $E_{N,k}(x)$ previously summarized in the introduction by equations (1.5)–(1.6).

We conclude this section by noting that if the term $\delta_{N,K}(x)$ is neglected in (3.4), then we obtain the two-parameter family of approximations (1.3). It follows that the accuracy of (1.3) depends on the magnitude of $\delta_{N,K}(x)$ as detailed below.

4. Selecting the accuracy control parameters N and K

In this section we present a method for selecting values for the integers $N \geqslant 1$ and $K \geqslant 0$ so that the basic approximation (1.3) enjoys D-decimal place accuracy on $(-\infty, \infty)$:

$$\left|\pi^{1/2}\chi(x) - \left[S_N(x) + E_{N,K}(x)\right]\right| = \left|\delta_{N,K}(x)\right| \leqslant 10^{-D}, \quad -\infty < x < \infty.$$

By (3.5) we have

$$\left|\delta_{N,K}(x)\right| \leqslant \int_0^\infty t^{1/2} e^{-2N\pi t}\left|\operatorname{csch} \pi t - C_K(t)\right| \mathrm{d}t. \tag{4.1}$$

Using (3.1) it can be verified that

$$\left|\operatorname{csch} \pi t - C_K(t)\right| \leqslant |a_{K+1}|\pi^{2K+1}t^{2K+1}, \quad t > 0.$$

Substituting the right-hand side of this inequality into the integrand in (4.1) and evaluating the resulting integral yields the upper bound

$$\left|\pi^{1/2}\chi(x) - \left[S_N(x) + E_{N,K}(x)\right]\right| \leqslant M_{N,K}, \quad -\infty < x < \infty, \tag{4.2}$$

where

$$M_{N,K} = |a_{K+1}|\frac{\sqrt{2}}{8}\frac{\Gamma(2k+5/2)}{N^{2K+5/2}4^K\pi^{3/2}}.$$

Using the well-known relationship

$$\frac{|B_{2n}|}{(2n)!} = \frac{2\zeta(2n)}{(2\pi)^{2n}}$$

in the definition of a_n following (3.1), we may write the above expression for $M_{N,K}$ in the form

$$M_{N,K} = \frac{\Gamma(2k+5/2)\zeta(2k+2)(1-2^{-2K-1})}{N^{2K+5/2}2^{2K+3/2}\pi^{2K+7/2}}. \tag{4.3}$$

In view of the uniform bound (4.2), we can obtain D decimal digits of accuracy in the approximation (1.3) for $-\infty < x < \infty$ if we choose the integer parameters $N \geqslant 1$ and $K \geqslant 0$ so that

$$-\log_{10} M_{N,K} = D. \tag{4.4}$$

In figure 3 we plot the contour curves (4.4) for $D = 3, 4, \ldots, 16$.

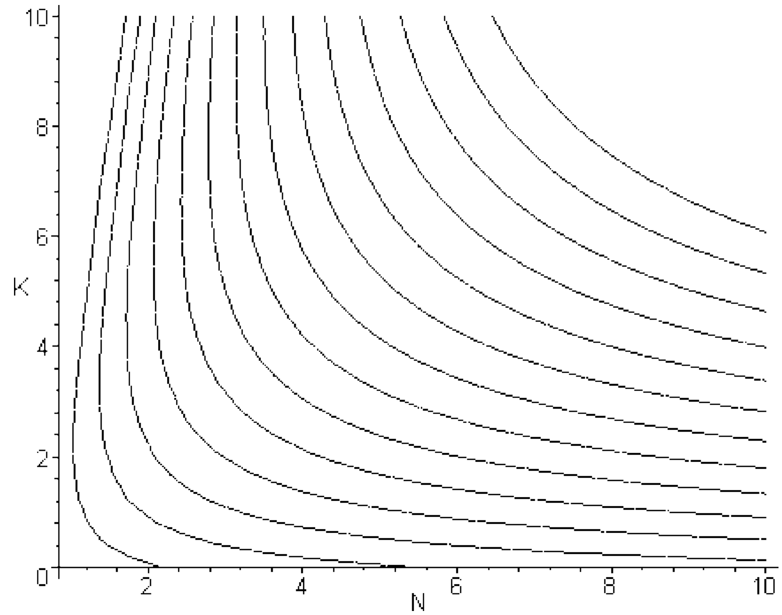

Figure 3. $-\log_{10} M_{N,K} = D$ for $D = 3, 4, \ldots, 16$ (top left to right curves).

Using figure 3 it is easy to select among several possible pairs N, K on the contour of level D, to insure that (1.3) achieves D decimal places of accuracy over the domain of $\pi^{1/2}\chi(x)$. For example, if $D = 4$ then the second curve from the top left in figure 3 shows that the choices $N = 2$, $K = 1$ are appropriate, whereas if $D = 15$ the choices $N = 8$, $K = 7$ are satisfactory. Notice that the predicted maximum absolute error of 10^{-15} in the latter case is consistent with the actual absolute error $0.25 \cdot 10^{-15}$ shown in figure 2.

5. Concluding remarks

The family of approximations defined by (1.3)–(1.6) give a useful method for computing $\pi^{1/2}\chi(x)$ on the domain $(-\infty, \infty)$. Table 1 gives closed forms for the coefficients d_k required in (1.5) for the cases when $K \leqslant 7$ in (1.3). The contour curves in figure 3 facilitate the selection of the accuracy parameters N and K to insure that (1.3) achieves D decimal digits of accuracy.

Appendix

One method for deriving the paramount integral representation (2.1) is based on the theory of special functions. Our starting point is Joncquière's function [10]

$$F(z, s) = \sum_{n=1}^{\infty} \frac{z^n}{n^s}$$

and Joncquière's relation

$$F(z,s) + e^{is\pi} F\left(\frac{1}{z}, s\right) = \frac{(2\pi)^s}{\Gamma(s)} e^{is\pi/2} \zeta\left(1 - s, \frac{\log z}{2\pi i}\right).$$

In view of the Reinmuth series representation (1.1) we see that the Randles–Sevcik function can be expressed in terms of Joncquière's function through

$$\pi^{1/2}\chi(x) = -F\left(-e^x, -\frac{1}{2}\right).$$

This later connection and Joncquière's relation implies that

$$\pi^{1/2}\chi(x) - i\pi^{1/2}\chi(-x) = \frac{\sqrt{2}}{4\pi} e^{-i\pi/4} \zeta\left(\frac{3}{2}, \frac{1}{2} - \frac{ix}{2\pi}\right).$$

Taking the real part of both sides of this last equation and employing the integral representation for the generalized zeta (Hurwitz) function given in [10] to represent $\zeta(3/2, 1/2 - (ix)/(2\pi))$, we obtain the form for $\pi^{1/2}\chi(x)$ given by (2.1).

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