

## IUPAC Recommendations

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# Definition of the transfer coefficient in electrochemistry (IUPAC Recommendations 2014)<sup>1</sup>

**Abstract:** The transfer coefficient  $\alpha$  is a quantity that is commonly employed in the kinetic investigation of electrode processes. An unambiguous definition of the transfer coefficient, independent of any mechanistic consideration and exclusively based on experimental data, is proposed. The cathodic transfer coefficient  $\alpha_c$  is defined as  $-(RT/F)(d\ln|j_c|/dE)$ , where  $j_c$  is the cathodic current density corrected for any changes in the reactant concentration on the electrode surface with respect to its bulk value,  $E$  is the applied electric potential, and  $R$ ,  $T$ , and  $F$  have their usual significance. The anodic transfer coefficient  $\alpha_a$  is defined similarly, by simply replacing  $j_c$  with the anodic current density and the minus sign with the plus sign. This recommendation aims at clarifying and improving the definition of the transfer coefficient reported in the 3<sup>rd</sup> edition of the IUPAC Green Book.

**Keywords:** electrode kinetics; IUPAC Physical and Biophysical Chemistry Division; symmetry factor; Tafel slope; transfer coefficient.

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## 1 Preamble

The task group recommends the definition of the transfer coefficient given in the next section. This is followed by a brief section that summarizes the reasons why this definition differs from that presently reported in the 3<sup>rd</sup> edition of IUPAC Green Book [1] and in some textbooks [2–5], and also from the different definition reported in the IUPAC Gold Book [6]. The task group has also produced a comprehensive technical report where the rationale behind the recommended definition is thoroughly described. The technical report immediately precedes this recommendation [7].

## 2 Definition

The anodic transfer coefficient  $\alpha_a$  and the cathodic transfer coefficient  $\alpha_c$  are defined by the following equations:

$$\alpha_a = (RT/F)(d\ln j_a / dE); \quad \alpha_c = -(RT/F)(d\ln |j_c| / dE) \quad (1)$$

In these equations,  $j_a$  and  $j_c$  are the anodic and cathodic current densities, respectively, corrected for any changes in the reactant concentration at the electrode surface with respect to its bulk value; incidentally, the symbols  $\ln j_a$  and  $\ln |j_c|$  imply that the argument of the logarithm is of dimension one, obtained by division with the corresponding unit, e.g.,  $\ln j_a$  meaning  $\ln(j_a/A\text{ m}^{-2})$ , and similarly for the other quantities  $|j_c|$ ,  $k_a$ , and  $k_c$ .  $E$  is the applied electric potential,  $R$  is the gas constant,  $T$  is the thermodynamic temperature, and  $F$  is the Faraday constant. In practice,  $\alpha_a$  and  $\alpha_c$  are defined as the reciprocal of the corresponding Tafel slopes,  $dE/d\ln j_a$  and  $-dE/d\ln |j_c|$ , made dimensionless by the multiplying factor  $RT/F$ . Both the transfer coefficient and the Tafel slope are determined at constant temperature and pressure.

### 3 Rationale behind the recommended definition

The definition of the cathodic transfer coefficient as recommended herein differs from that reported in the IUPAC Green Book,  $\alpha_c = -(RT/nF)(d\ln k_c/dE)$ , in two points: (1) the electroreduction rate constant  $k_c$  is replaced by the cathodic current density  $j_c$  corrected for any changes in the reactant concentration at the electrode surface with respect to its bulk value; (2) the number  $n$  of electrons is removed. For the sake of simplicity, the following considerations will refer to the cathodic transfer coefficient  $\alpha_c$ , but they can be readily extended to the anodic transfer coefficient  $\alpha_a$ ; it is just sufficient to replace the minus sign by the plus sign in front of the definition of the transfer coefficient, the cathodic current density  $j_c$  by the anodic current density  $j_a$ , and the release of electrons from the electrode by their uptake.

With respect to the first change, the rate constant  $k_c$  differs from the current density  $j_c$  by a constant multiplying factor. Since this constant factor vanishes when differentiating the logarithm of  $k_c$  to obtain  $\alpha_c$ , strictly speaking, the first change is irrelevant. Nonetheless, the determination of  $k_c$  requires a correction for any change in the reactant concentration at the electrode surface, which in turn depends on the particular electrochemical perturbation imposed on the system. In some cases, the equations adopted to determine the rate of change of  $\ln k_c$  with potential are roughly approximate, and they may also account for diffuse layer effects by using the Frumkin correction factor [8, 9]. It is, therefore, deemed more convenient not to bind the definition of the transfer coefficient to the more or less rigorous equations used to determine  $k_c$ , by simply referring to the current density  $j_c$  “corrected for any changes in the reactant concentration at the electrode surface with respect to its bulk value”. In this way, the unavoidable amount of arbitrariness involved in this correction is manifest, instead of being hidden in the procedure adopted to determine  $k_c$ .

The second change, consisting in the removal of the number  $n$ , is based on the following considerations. From a purely experimental point of view, what can be directly measured is the slope of the plot of  $E$  against  $-\ln |j_c|$  (provided this slope is constant over a current range of at least one order of magnitude), i.e., the so-called *Tafel slope*, or its reciprocal,  $-d\ln |j_c|/dE$ . According to the recommended definition of the cathodic transfer coefficient  $\alpha_c$ , its value is obtained by simply multiplying the directly measurable quantity  $-d\ln |j_c|/dE$  by  $RT/F$ , to make it dimensionless. According to the definition in the 3<sup>rd</sup> edition of the Green Book, this quantity is regarded as equal to the product,  $\alpha n$ , of the two distinct quantities  $\alpha$  and  $n$ ; one is, therefore, faced with the necessity of estimating both quantities separately, on the basis of some mechanistic considerations. This may generate misleading conclusions. A frequently adopted approach consists in regarding *a priori*  $\alpha_c$  as equal to a *symmetry factor*  $\beta = 0.5$  in order to extract a value of  $n$ , which is then identified with the number of electrons involved in the rate-determining step of the electrode process. If  $n$  is close to an integer, it is rounded off to this integer, thus allowing for a deviation of  $\beta$  from the 0.5 value. The  $\beta$  value may indeed deviate from 0.5 to some extent, and it may also vary with potential over a sufficiently broad potential range. This approach is formally correct only if the electrode process consists of a single elementary step involving the simultaneous release of  $n$  electrons from the electrode to the reactant. In many cases, an electrode process consists of a sequence of consecutive (or even parallel) elementary electron-transfer steps and chemical steps. Under these conditions, the above approach can still be regarded as formally correct only if the

first elementary step of the sequence determines the rate of the whole process and involves the simultaneous release of  $n$  electrons from the electrode.

There is a further restriction imposed on this approach by the Marcus theory of electron transfer, first formulated in 1956 [10–12]. In view of this theory and of the subsequent quantum mechanical theory of the kinetics of the elementary act of an electrochemical process in polar liquids developed by Levich, Dogonadze, Kuznetsov, and others [13], it is now clear that the simultaneous transfer of more than one electron to or from an electrode is highly improbable. Nowadays, only a few of the previously cited examples of simultaneous transfer of two electrons between species in solution can be regarded as possible. In view of this further restriction, equating the experimental quantity  $-(RT/F)(d\ln k_c/dE)$  to a product  $\alpha n$  from which the  $n$  value is extracted by setting *a priori*  $\alpha \approx 0.5$  can lead to an acceptable result only if  $n$  turns out to be equal to unity. When the  $n$  value obtained by this approach is greater than unity, identifying  $n$  with the number of electrons involved in an unspecified rate-determining step is unwarranted. Equally unwarranted is the identification of  $n$  with the number of electrons involved in the overall electrode reaction as written, a number commonly denoted in the literature by the same symbol. Thus, e.g., in a multistep electrode process consisting of a series of consecutive elementary steps, the electrode kinetics is only affected by the rate-determining step and by the steps that precede it, while it is blind to the subsequent steps, which may well involve further electron transfers.

The definition of the transfer coefficient as recommended herein is based exclusively on a directly determined experimental quantity, independent of any mechanistic consideration on the electrode process under investigation. In particular, it does not require *a priori* assumptions about the  $\alpha$  value required to estimate the multiplying factor  $n$ . Conversely, the  $\alpha_c$  value directly obtained from the expression  $-(RT/F)(d\ln |j_c|/dE)$  can be profitably compared *a posteriori* with values of this quantity calculated for different electrode reaction mechanisms in order to sort that (or those) in best agreement with the experimental  $\alpha_c$  value. Determining the reaction mechanism remains a quite demanding task, but the definition as proposed herein at least prevents an unjustified *a priori* assumption on the  $n$  value from invalidating the mechanism from the very beginning. Finally, it should be mentioned that the present definition of the transfer coefficient is not new, and has been reported in textbooks [14–16] and monographs [17] and adopted by many electrochemists for the elucidation of the mechanism of electrode processes.

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