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Short communication

Fourty years of the Šesták–Berggren equation

Peter Šimon*

Institute of Physical Chemistry and Chemical Physics, Faculty of Chemical and Food Technology, Slovak University of Technology, Radlinského 9, SK-812 37, Bratislava, Slovak Republic

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ABSTRACT

The Šesták–Berggren equation, representing a powerful tool for the description of kinetic data by the model-fitting methods, is analyzed. It is discussed that the exponents in the conversion function are non-integer in general and that the conversion function may not have a mechanistic interpretation. Within the framework of single-step approximation, the Šesták–Berggren equation enables to describe the kinetics of complex condensed-state processes without a deeper insight into their mechanism.

Kinetics of the processes in condensed phase is frequently described by the so-called general rate equation representing the reaction rate $\mathrm{d}\alpha/\mathrm{d}t$ as a product of two mutually independent functions:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = k(T)f(\alpha) \tag{1}$$

The temperature function, $k(T)$, depends solely on temperature T and the conversion function, $f(\alpha)$, depends only on the conversion of the process, α. The temperature function is prevailingly interpreted as the rate constant and the conversion function is believed to reflect the mechanism of the process.

Fourty years ago, a paper by Šesták and Berggren [1] appeared in this journal introducing in Eq. (1) a three-parameter conversion function for a generalized description of reaction kinetics. The equation is often named after their authors, i.e. the Šesták–Berggren equation (habitually abbreviated as the SB equation):

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = k(T)\alpha^m(1-\alpha)^n\,[-] \tag{2}$$

where m, n, and p are the (generally non-integer) exponents. Later on, Gorbachev [2] demonstrated that, for isothermal conditions, Eq. (2) can be transformed into three invariant expressions with two exponents only. Among them, the following form is the one which is most frequently employed:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = k(T)\alpha^a(1-\alpha)^b \tag{3}$$

The exponents a and b in Eq. (3) may differ from those m and n introduced in Eq. (2).

Eq. (3) can be encountered in the literature published before 1971. Erofeev and Mitskevich in 1961 [3] pointed out that the expansion and rearrangement of the differentiated form of the Yerofeev equation lead to Eq. (3). As early as in 1940, Akulov reported Eq. (3) where the constants a and b called the "constants of homogeneity" [4]. Eq. (3) is also quite frequently cited in the literature as an extended form of the Prout and Tompkins autocatalytic equation [5], for example in [6–9]. Nonetheless, Eq. (3) is generally considered a transformation of Eq. (2) so that it is equally called the SB equation.

Eq. (3) is widely applied to the study of not only isothermal, but also non-isothermal processes; mathematical correctness of either description was justified in [10]. Later it was shown [11] that this two-parameter model retains its physical meaning only for $a \leq 1$. Málek pointed out that the classical nucleation-growth equation (often abbreviated as JMAYK) is actually a special case of this two-parameter SB model and thus SB equation represents a plausible alternative description for the crystallization processes taking place in non-crystalline solids [12]. The increasing value of the exponent a indicates a more important role of the precipitated phase on the overall kinetics. It also appears that a higher value of the second exponent ($b > 1$) indicates increasing reaction complexity; however, the temptation to relate the values of a and b to a reaction mechanism can be doubtful and should be avoided [12] without complementary measurements [13,14].

Due to its ability to describe variety of kinetic data both of organic and inorganic origin [9], the SB equation attracts much attention. It was believed that it can be considered a universal expression for kinetic models [15]. For certain combinations

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* Tel.: +421 2 59325530; fax: +421 2 52926032.
E-mail address: peter.simon@stuba.sk

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of exponents, the conversion function in SB equation can merge in most conversion functions representing mechanisms of processes. For further improvement of the mechanistic interpretation, multiplying the SB equation by an accommodation constant was suggested [16]. Nevertheless, it was recognized that kinetic models of solid-state reactions are often based on a formal description of geometrically well-defined bodies under isothermal conditions; for real processes, these assumptions are evidently incorrect [17].

In contrast with the mechanistic interpretations of Eq. (1) mentioned above, there is the idea of the single-step approximation [18,19]. The history and contradictions of the concept of single-step reaction have been discussed in [20]. The approximation is based on the fact that the processes in condensed phase tend to occur in multiple steps that have different rates. Each reaction step should be described by its own kinetic equation. It has been demonstrated that, neither for the simplest cases, the kinetic equations characterizing complex mechanisms cannot be reduced into the factorized form of Eq. (1) [21]. Hence, it has been concluded that Eq. (1) is not a true kinetic equation; it is just a mathematical tool for the description of kinetic data [18,19,21]. The single-step approximation resides in replacing the set of differential rate equations by the single-step generalized rate equation. The functions $k(T)$ and $f(\alpha)$ represent, in general, just the temperature and conversion components of the kinetic hypersurface; this hypersurface is a dependence of conversion as a function of time and temperature [18]. Thus, the temperature function may not be the rate constant and the conversion function may not reflect the reaction mechanism.

The value and wide applicability of the SB equation surpasses in the light of the single-step approximation. The conversion functions in Eqs. (2) or (3) are able to describe both the S-shaped accelerating kinetic curves and the n-th order ones. Due to the possibility of adjustment of the exponents, the function is very versatile and flexible. In general, the values of exponents may not reflect the reaction mechanism; on the other hand, they enable to describe kinetic data and modeling the kinetics of the overall process without a deeper insight into its mechanism. The SB equation provides purely formal description of the kinetics and it should be applied and understood in this way.

The Šesták–Berggren equation represents a powerful tool for the description of kinetic data by the model-fitting methods. According to SCOPUS, the paper [1] was cited 316 times since 1996. Since 1971, the paper was cited nearly 600 times and probably is the most cited paper in the history of almost twenty two thousand papers published in Thermochimica Acta. There are no doubts that the SB equation will continue being widely applied also in future, either in the form of Eq. (2) or Eq. (3).

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