

ON THE $p(x)$ APPROXIMATION IN THE NON-ISOTHERMAL REACTION KINETICS BY A GENERALIZED EXPONENTIAL INTEGRAL The Concept

by

Jordan HRISTOV and Veronika KARADJOVA*

^a Department of Chemical Engineering, University of Chemical Technology and Metallurgy,
Sofia, Bulgaria

^b Department of Inorganic Chemistry, University of Chemical Technology and Metallurgy,
Sofia, Bulgaria

Original scientific paper
<https://doi.org/10.2298/TSCI21S2321H>

A non-Arrhenius model based on the Mittag-Leffler function has been conceived as a basic concept. This approach allows modelling both sub-Arrhenius and super-Arrhenius behaviours and giving rise to modified temperature integrals.

Key words: non-Arrhenius, Mittag-Leffler function, temperature integral

Introduction

The temperature integral is a main tool for data treatment in thermal analysis of reaction kinetics involving the Arrhenius exponential dependence of the rate constant of the temperature, T , namely:

$$\frac{da}{dt} = K(T)f(a), \quad K(T) = A_0 e^{-\frac{E}{RT}} \quad (1)$$

where a is the fraction decomposed, T – the absolute temperature, and $f(a)$ – the conversion function, depending on the geometry commonly expressed in a general form as $f(a) = a^m(1-a)^n$. With a linear heating rate $dT/dt = b$, applying the Arrhenius equation and integration (1) can be transformed as:

$$\frac{da}{dT} = \frac{K(T)}{b} f(a) \Rightarrow \frac{da}{f(a)} = \frac{K(T)}{b} dT \Rightarrow \int_0^a \frac{da}{f(a)} = \frac{A_0}{b} \int_0^T e^{-\frac{E}{RT}} dT \quad (2)$$

where the lower terminal in the last version of (2) can be taken as zero for practical purposes (if the reaction starts at a temperature where its rate extremely slow) [1, 2].

The temperature integral

Changing the variable as $x = E/RT$ in the integral and its terminals, we may integrate (2) over the time-dependent temperature range thus defining the function $p(x) = p(E/RT)$ (temperature integral) [2-4]:

* Corresponding author, e-mail: vkar@mail.bg

$$\int_x^\infty \frac{e^{-x}}{x^2} dx = p(x) = \frac{e^{-x}}{x} - \int_x^\infty \frac{e^{-x}}{x} dx \quad (3)$$

Because in the variable $x = E/RT$ the ratio E/R is temperature-independent (the activation energy is temperature-independent), then $x \equiv 1/T$. The last (second) term in $p(x)$ the so-called *exponential integral* commonly denoted as $Ei(x)$ (included as a special function in MAPLE and MATHEMATICA) defined [5]:

$$Ei(x) = \int_{-x}^\infty \frac{e^{-x}}{x} dx = - \int_{-\infty}^x \frac{e^{-x}}{x} dx, \quad x > 0, \quad x \in C^{-1} \quad (4)$$

Moreover, the following identities involving the incomplete Gamma function (5) holds [5]:

$$\Gamma(\nu, x) = \int_x^\infty u^{\nu-1} e^{-u} du, \quad Ei^*(z) = -Ei(-z) = \Gamma(0, x) = \int_x^\infty \frac{e^{-u}}{u} du, \quad \nu \in R, \quad x \in C^{-1} \quad (5)$$

where we have [5] $Ei^*(0) = +\infty$, $Ei^*(\infty) = 0$, and $Ei^*(-\infty) = -\infty$. The integration in (4) cannot be obtained analytically and thus various approximations are widely used, among them: Following Coulson and Duncanson [6] the following series expansion hold:

$$Ei^*(x) = -Ei(-x) = -\gamma - \log x + \sum_{n=1}^\infty \frac{(-1)^{n-1} x^n}{n.n!}, \quad < 15 \quad (6)$$

where $\gamma = 0.577216\dots$ is the Euler-Mascheroni constant.

However, it has been especially mentioned in [6] that none of these approximations is particularly convenient in the range $15 < x < 25$. According to Sestak [4] a convergent series:

$$Ei(x)\gamma + \ln x^4 - x + \frac{x}{2.2!} - \dots + \frac{(-1)x^n}{n.n!} = 0.577216 + \ln x^4 + \sum_{n=1}^N \frac{(-1)^n x^n}{n.n!} \quad (7)$$

or a semi-convergent series obtained by integration by parts as $Ei(x)$ approximated:

$$Ei(x) \approx \frac{e^{-x}}{x} \left[1 - \frac{1}{x} + \frac{2!}{x^2} - \dots + \frac{(-1)n!}{x^n} = \sum_{n=0}^N \frac{(-1)^n n!}{x^n} \right] \quad (8)$$

can be successfully applied to model experimental data and recover the kinetics parameters such as A_0 and the activation energy, E . By the revers distribution $(1/x)$ in (3) the following successful approximations of Schoelmilch [7], see also [3, 4, 6] is widely applied in solid kinetic studies:

$$Ei = \frac{e^{-x}}{x} \left[1 - \frac{1}{x+1} + \frac{1}{(x+1)(x+2)} - \dots + \frac{(-1)^n}{(x+1)\dots(x+n)} \right], \quad -x > 15 \quad (9)$$

and consequently, in (9) a_n is a constant:

$$p(x) = \frac{e^{-x}}{x(x+1)} \left[1 - \frac{1}{x+2} + \frac{1}{(x+2)(x+3)} - \dots + \frac{(-1)^{n+1} a_n}{(x+2)\dots(x+n)} \right] \quad (10)$$

There are many approximations working in different ranges of variations of the variable x , see the excellent review of Flynn [3]. But, following the main idea developed in this article we stress the attention on problems emerging from the postulated exponential form of the Arrhenius equation (see the next section), which actually is the genesis of the temperature (exponential) integral discussed here.

Arrhenius equation: emerging problems

The canonical exponential Arrhenius law (1) in logarithmic co-ordinates should give a straight line, there are many cases when the experimental curves do not confirm this linear behaviour and they are referred as non-Arrhenius [8-11]. In such a case a generalization by the Kohlrausch exponential was conceived by Fang [8, 9], namely (in terms of the present article):

$$K = A_0 \exp \left[- \left(\frac{E}{RT} \right)^\beta \right], \quad 0 < \beta \leq 1 \quad (11)$$

which for $\beta = 1$ recovers the Arrhenius relationship. It is noteworthy to mention that the Kohlrausch function has a series approximation as a special case of the Mittag-Leffler function [12]:

$$e^{-at} = E_{\gamma=1}(-at) = \sum_{n=0}^{\infty} \frac{(-at)^n}{\Gamma(\gamma n + 1)} = \sum_{n=0}^{\infty} \frac{(-at)^n}{n!} = \sum_{n=0}^{\infty} \frac{(-at)^n}{\Gamma(n+1)} \quad (12)$$

Motivation and aim

The main motivation of this work envisages modelling non-Arrhenius kinetic and especially the calculation of the temperature integral. The main inspiration comes from the authors experience in fractional calculus where the exponential function is only a special case of the Mittag-Leffler function as well the series approximation of the Kohlrausch function. But, the driving impulse was the excellent work on Mainardi and Massina [5] on a generalization of $Ei(x)$ in the sense of the construction of the Schelkunoff integral [13]:

$$Ei_n(x) = \int_0^x \frac{1 - e^{-u}}{u} du, \quad x \in C$$

The only aim of this work is to construct a rate constant $K(T)$ based on the Mittag-Leffler function of one parameter, thus conceiving a concept of a temperature integral, *i.e.* the $p(x)$ function, as a power-law series relevant to non-Arrhenius (precisely sub-Arrhenius cases).

Modified non-Arrhenius rate constant $K(T)$ based on $E_\alpha(x)$ function

Based on the presented motivation and background problems commented, this work conceives a non-Arrhenius functional relationship of the temperature dependent rate constant $K(T)$:

$$K_{NA}(T) = A_N E_\alpha(-x), \quad x = E/RT, \quad E_\alpha(-x) = \sum_{k=0}^{+\infty} \frac{(-1)^k x^k}{\Gamma(k\alpha + 1)}, \quad 0 < \alpha < 1 \quad (13)$$

where for $\alpha = 1$ the exponential relationship (1) is recovered. Hence, the power x^k should be $x = (E/R)^k (1/T)^k$ and has an unchangeable coefficient $(E/R)^k$:

$$E_{\alpha}(-x) = \sum_{k=0}^{+\infty} \eta^k \frac{(-1)^k x^k}{\Gamma(k\alpha + 1)}, \quad \eta = \frac{E}{R} \quad (14)$$

Expressing (13) in dimensionless forms as $[K_{NA}(T)]/A_N = \exp(-x)$ we get the plots in fig. 1(a) with sub-Arrhenius and super-Arrhenius plots as well as analogous behaviour of the modified relationship $[K_{NA}(T)]/A_N = E_{\alpha}(-x)$, plotted for different values of α , see fig. 1(b). The plots in fig. 1(b) reveal that varying the fractional parameter all lines are above the exponential line (sub-exponential behaviour) line beyond a certain value of x , while for small x , there is short range with a super-exponential behavior. See similar plots in [14, 15]. This strongly indicates that by this modification of the non-Arrhenius relationship a *sub-Arrhenius kinetics* can be modelled. Therefore, the main question at this moment is: where (for which x the behaviour changes from super-exponential to sub-exponential? If we try to solve the equation:

$$E_{\alpha}(-x) = \exp(-x) \Rightarrow \frac{s^{-1}}{s^{\alpha} - 1} = \frac{1}{s + 1}$$

the trivial solution is for $\alpha = 1$. However, if we look at the range when $x < 1$ and $x \rightarrow 0$ we may use the approximation [14, 15] $E_{\alpha}^0(-x^{\alpha}) \equiv \exp[-x^{\alpha}/\Gamma(1+\alpha)]$. Then, from the equation $e^{-x^{\alpha}/\Gamma(1+\alpha)} = -e^{-x}$ it follows that $x^{\alpha}/\Gamma(1+\alpha) = 1$ and consequently $x \approx [\Gamma(1+\alpha)]^{1/\alpha}$. Bearing in mind that $\Gamma(1+\alpha) \sim O(1)$ for $0 < \alpha < 1$ then the transient points for different α are also of order of magnitude of unity, as it is indicated by the plots. These approximate estimates are in agreement with the results of Haupt and Lion [16], see fig. 2 in [16] where for all α and $0 < x < 1$ the behaviour is super-exponential. However, in general the function $E_{\alpha}(-x)$ for $x > 1$ exhibits behaviours that can be employed in modelling of sub-Arrhenius kinetics.

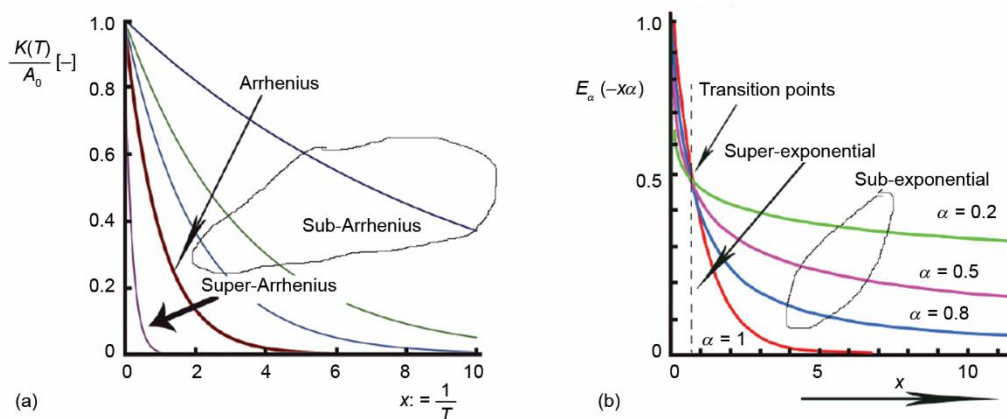


Figure 1. Versions of non-Arrhenius behavior; (a) with sub-Arrhenius and super-Arrhenius areas and analogous behaviour of the Mittag-Leffler function $E_{\alpha}(-x^{\alpha})$ and (b) with sub-exponential and super-exponential trends

Temperature integral of $K_{NA}(T)$

Now, the focus is on the function $p(x)$ (the modified temperature integral) generated by the modified exponential integral. With $K_{NA}(T)$ defined by (13) the temperature integral takes the forms:

$$\int_x^\infty \frac{E_\alpha(-x)}{x^2} dx = P_{NA1}(x) = \int_x^\infty \sum_{k=0}^\infty \frac{(-1)^k x^{k-2}}{\Gamma(\alpha k + 1)} dx = (-\gamma - \ln x) + \left[\sum_{k=2}^\infty \frac{(-1)^k x^{k-1}}{(k-1)\Gamma(\alpha k + 1)} \right]_x^\infty \quad (15)$$

Alternatively, there is an option for an ad hoc construction concerning the Mittag-Leffler function $E_\alpha(-x)$ to be used only in the second term of temperature integral, see (3), namely:

$$P_{NA2}(x) = \frac{e^{-x}}{x} - \int_x^\infty \frac{E_\alpha(-x)}{x} dx = \frac{e^{-x}}{x} - \int_x^\infty \sum_{k=0}^\infty \frac{(-1)^k x^{k-1}}{\Gamma(\alpha k + 1)} dx =$$

$$(\gamma + \ln x) + \frac{e^{-x}}{x} + \sum_{k=2}^\infty \frac{(-1)^k x^k}{k\Gamma(\alpha k + 1)} dx \quad (16)$$

Hence, we artificially introduced the non-Arrhenius behavior in second term of the temperature integral $p(x)$, but not in its initial formulation:

$$\int_x^\infty \frac{e^{-x}}{x^2} dx$$

as it was done in the case of $P_{NA1}(x)$. For $\alpha = 1$, the final form of the denominator $k\Gamma(k+1) = k.k!$ that coincides with the approximations (6) and (7). Comparative plots of two well-known approximations with $P_{NA1}(x)$ and $P_{NA2}(x)$ are shown in fig. 2(a) for the case with $\alpha = 1$, because only in this case we may compare all approximations considered here. It is remarkable that *ad hoc* modified function $P_{NA2}(x)$ is close to the well-known approximations, which is natural since for $\alpha = 1$, we get the classical temperature integral. Further, the variations of $P_{NA1}(x)$ for different α are shown in fig. 2(b) (this example for small x is mainly applicable to super-Arrhenius case since decrease in α shifts downward the lines). For now, it is hard to compare all these approximations in a common range of variations of x due to their different rates and magnitudes; as support of this standpoint see the plot of the Schloemilch approximation in fig. 2(c) where the order of magnitude varies from 10^{-10} up to 10^{-9} in a very short range of variations of x . But, in general, all approximations in fig. 2(a) exhibit similar trends with increase in x while discrepancies are mainly for small x (high T).

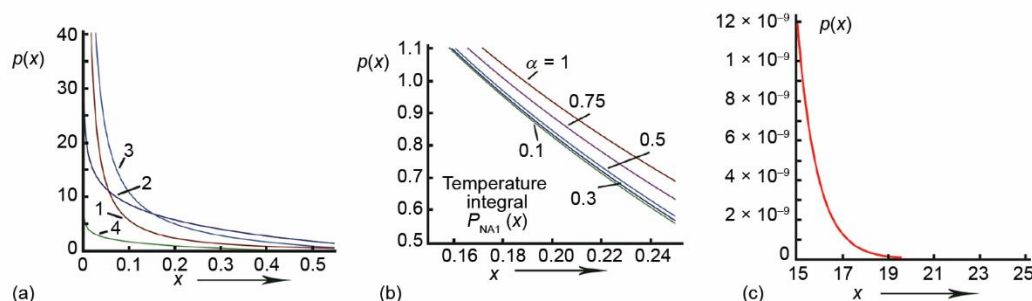


Figure 2. Comparative plots of well-known approximations of $p(x)$ with the new approximation $P_{NA1}(x)$ and $P_{NA2}(x)$; (a) 1 – Schloemilch, 2 – Sestak, eq. (7), 3 – $P_{NA2}(x)$, 4 – $P_{NA1}(x)$, (b) variations of $P_{NA1}(x)$ for different α , and (c) Schoemilch approximation

Final comments and questions

This short article conceives a concept towards formulation of a generalized Arrhenius relationship allowing to model both sub-Arrhenius and super-Arrhenius. The result reveals that is more suitable for sub-Arrhenius kinetics. Based on this initial steps we may formulate some it is more suitable this drawing some principle lines in the future development of the problem conceived here, as follows.

- As the first step, establishment of the ranges where approximation of sub-Arrhenius kinetics can be modelled adequately by $E_{\alpha}(-x)$.
- How variations in the fractional order α affect the accuracy of approximations and what type of techniques should be applied to recover its value from experimental data sets?
- Tests of developed temperature integrals to real experimental data (taken from both the literature and experiments) as well as comparisons with many approximations already existing in the literature

These remarks envisage what would be done, inspired by these first results, but actually the concept may provoke more studies and successful application of the $E_{\alpha}(-x)$ function in chemical kinetics.

References

- [1] Doyle, C. D., Kinetic Analysis of Thermogravimetric Data, *J. Appl. Polymer Sci.*, 5 (1961), 15, pp. 285-292
- [2] Madhusudanan, P. M., Krishnan, K., New Approximation for the $p(x)$ Function in the Evaluation of Non-Isothermal Kinetic Data, *Thermochim. Acta*, 97 (1986), 1, pp. 189-201
- [3] Flynn, J. H., The Temperature Integral-Its Use and Abuse, *Thermochim. Acta*, 300 (1997), 1-2, pp. 83-92
- [4] Sestak, J., On the Applicability of the $p(x)$ Function to the Determination of Reaction Kinetics Under Non-Isothermal Conditions, *Thermochim. Acta*, 3 (1970), 2, pp. 150-154
- [5] Mainardi, F., Masina, E., On Modification of the Exponential Integral with the Mittag-Leffler Function, *Frac. Calc. Appl. Anal.*, 21 (2018), 5, pp. 1156-169
- [6] Coulson, C. A., Duncanson, W. E., LXXX. Some New Values for the Exponential Integral, *The London, Edinburgh, and Dublin Philosophical Magazine and Journal of Science*, 33 (1942), 225, pp. 754-761
- [7] Shoelmich, O., *Vorlesungen uber hohere analysis*, vol. II, Braunschweig, Germany, 1874, p. 269
- [8] Fang, P. H., Arrhenius Relation and Its Fractalization, *Z. Phys. Chem*, 219 (2005), 6, pp. 831-836
- [9] Fang, P. H., Kohlrausch and Arrhenius Analysis for Some Solid and Liquid Materials, *J. Non-Crystalline Solids*, 354 (2008), 10-11, pp. 989-993
- [10] Leon, C., et al., Non-Arrhenius Conductivity in the Fast Ionic Conductor $\text{Li}_{0.5}\text{La}_{0.5}\text{TiO}_3$: Reconciling Spin-Lattice and Electrical-Conductivity Relaxations, *Phys. Rev. B*, 56 (1997), 9, pp. 5302-5305
- [11] Rivera, A., et al., Temperature Dependence of the Ionic Conductivity in $\text{Li}_{3x}\text{La}_{2/3-x}\text{TiO}_3$: Arrhenius vs. Non-Arrhenius, *Appl. Phys. Lett.*, 82 (2003), 15, pp. 2425-2427
- [12] Berberan-Santos, M. N., et al., Luminescence Decays with Underlying Distributions of Rate Constants: General Properties and Selected Cases, in: *Fluorescence of Supramolecules, Polymers, and Nanosystems*, Berberan-Santos, M. N., Ed., Springer Ser., *Fluorescence*, 4, (2008), pp. 67-103
- [13] Schelkunoff, S. A., Proposed Symbols for the Modified Cosine and Exponential Integrals, *Quart. Appl. Math.*, 2 (1944), 1, p. 90
- [14] Mainardi, F., On Some Properties of the Mittag-Leffler function $E_{\alpha}(-t^{\alpha})$, Completely Monotone for $t > 0$ with $0 < \alpha < 1$, *Discrete Cont. Dyn. Syst.*, 19 (2014), 7, pp. 2267-2278
- [15] Mainardi, F., Why the Mittag-Leffler Function can be Considered the Queen Function of the Fractional Calculus? *Entropy*, 22 (2020), 12, ID 1359
- [16] Haupt, P., Lion, A., On Finite Linear Viscoelasticity of Incompressible Isotropic Materials, *Acta Mechanica*, 159, (2002), 1, pp. 87-124