Short Communications

INTEGRAL OF THE BOLTZMANN FACTOR
A new approximation

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Abstract

A new approximation is proposed to the integral of the Boltzmann factor:

$$\int_0^T e^{-E/RT} dT$$

and is shown to be more accurate than the existing approximations over the entire range of values of E/RT, including low values.

Keywords: Boltzmann factor

Introduction

In the course of analyzing data collected from thermal analysis experiments, it often becomes necessary to evaluate the integral of the Boltzmann factor:

$$\Lambda(T) = \int_0^T e^{-E/RT} dT$$

As there is no exact closed-form solution to this integral, many approximations to it have been proposed over the years. Some of the more familiar ones are the following:

$$\text{Frank–Kamenetskii [1]: } \Lambda(T) = \frac{RT^2}{E} e^{-E/RT} \quad (1)$$

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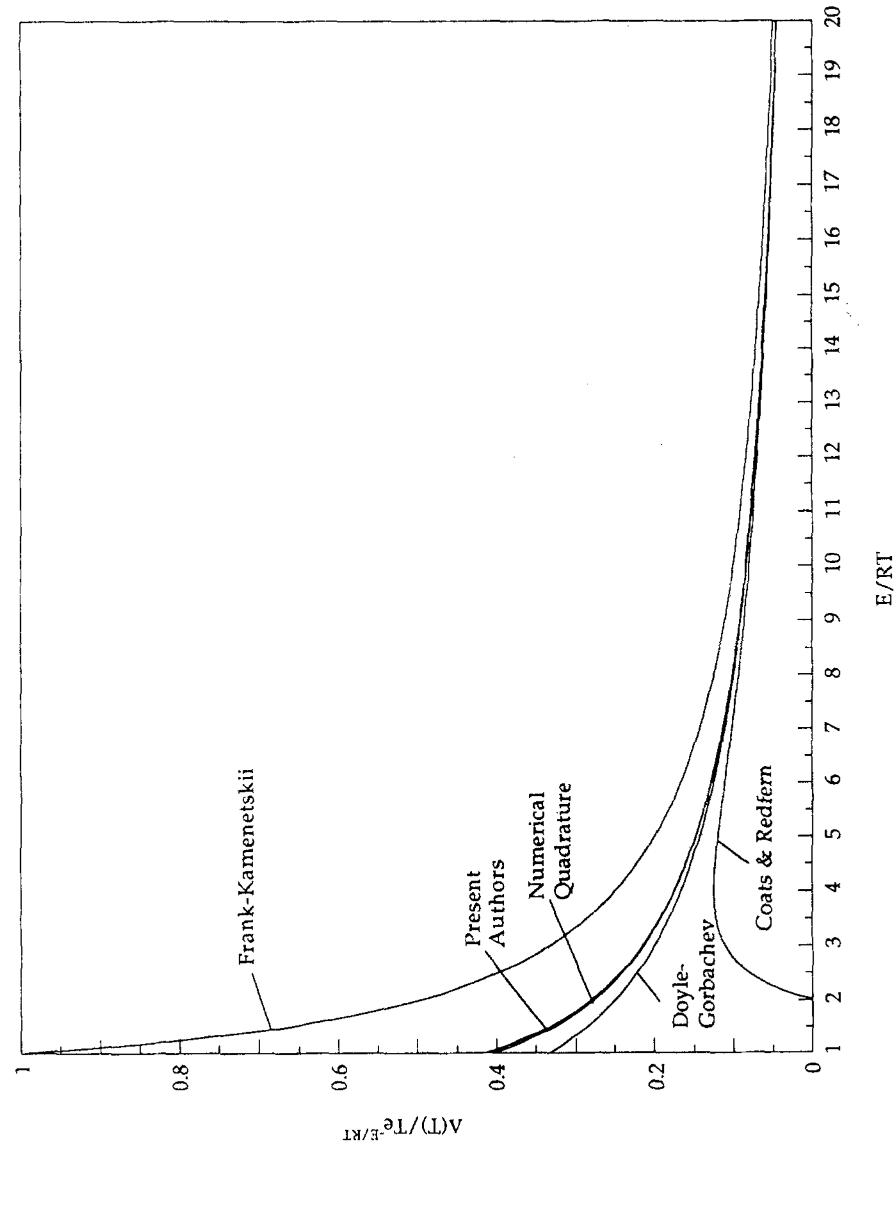

Fig. 1 Approximations to the integral of the Bolzmann factor

$$\text{Coats and Redfern [2]: } \Lambda(T) = \frac{RT^2}{E}\left[1 - \frac{2RT}{E}\right] e^{-E/RT} \tag{2}$$

$$\text{Gorbachev[3]: } \Lambda(T) = \frac{T}{E/RT + 2}\, e^{-E/RT} \tag{3}$$

In addition, asymptotic approximations to the integral are also available in the form of series. Based on the first three terms of the Schömilch series [4], Doyle [5] proposed an approximation that is identical to Eq. (3). Tables have also been published listing the values of the integral for different values of T and E/RT.

Discussion

In many instances such as, for example, combustion calculations where conservation equations have to be numerically integrated, it is convenient to have a closed-form expression for the approximation to the integral as in Eqs (1–3). Such an expression which is more accurate than the ones presently available, particularly at low values of E/RT often encountered in combustion phenomena, is derived below.

The approximation is written as:

$$\int_0^{T_f} e^{-E/RT} dT = \left[\frac{T}{E/RT + n}\, e^{-E/RT}\right]_0^{T_f} \tag{4}$$

where n, a function of E/RT_f, is a constant for given values of E and T_f. n is thus independent of T, but changes with T_f, the final temperature.

Differentiating Eq. (4) with respect to T and rearranging, we get:

$$e^{-E/RT} = \left[1 + \frac{2(E/Rt) - n(E/RT) + n - n^2}{(E/RT + n)^2}\right] e^{-E/RT} \tag{5}$$

We choose n such that Eq. (5) is satisfied at $T = T_f$ so that

$$n = \frac{1 - (E/RT_f) + \sqrt{(E/RT_f)^2 + 6(E/RT_f) + 1}}{2} \tag{6}$$

This ensures that the slopes of the function and the approximation match at $T = T_f$.

The approximation to the Boltzmann factor therefore turns out as:

$$\Lambda(T) = \frac{2Te^{-E/RT}}{1 + (E/RT) + \left\{(E/RT)^2 + 6(E/RT) + 1\right\}^{1/2}} \tag{7}$$

Table 1 Values of $\Lambda(T)/Te^{-E/RT}$

E/RT	Numerical quadrature	Present approximation Eq. (7)	Frank-Kamenetskii Eq. (1)	Coats and Redfern Eq. (2)	Gorbachev, Doyle Eq. (3)
1	4.037E–01	4.142E–01	1.000E+ 00	–1.000E+ 00	3.333E–01
2	2.773E–01	2.808E–01	5.000E–01	0.000E+ 00	2.500E–01
3	2.137E–01	2.153E–01	3.333E–01	1.111E–01	2.000E–01
4	1.746E–01	1.754E–01	2.500E–01	1.250E–01	1.667E–01
5	1.479E–01	1.483E–01	2.000E–01	1.200E–01	1.429E–01
6	1.284E–01	1.287E–01	1.667E–01	1.111E–01	1.250E–01
7	1.135E–01	1.137E–01	1.429E–01	1.020E–01	1.111E–01
8	1.018E–01	1.019E–01	1.250E–01	9.375E–02	1.000E–01
9	9.224E–02	9.233E–02	1.111E–01	8.642E–02	9.091E–02
10	8.437E–02	8.443E–02	1.000E–01	8.000E–02	8.333E–02
11	7.774E–02	7.779E–02	9.091E–02	7.438E–02	7.692E–02
12	7.209E–02	7.212E–02	8.333E–02	6.944E–02	7.143E–02
13	6.720E–02	6.723E–02	7.692E–02	6.509E–02	6.667E–02
14	6.294E–02	6.297E–02	7.143E–02	6.122E–02	6.250E–02
15	5.920E–02	5.921E–02	6.667E–02	5.778E–02	5.882E–02
16	5.587E–02	5.588E–02	6.250E–02	5.469E–02	5.556E–02
17	5.290E–02	5.291E–02	5.882E–02	5.190E–02	5.263E–02
18	5.023E–02	5.024E–02	5.556E–02	4.938E–02	5.000E–02
19	4.782E–02	4.783E–02	5.263E–02	4.709E–02	4.762E–02
20	4.563E–02	4.564E–02	5.000E–02	4.500E–02	4.545E–02

Table 1 compares the values of $\Lambda(T)/Te^{-E/RT}$ for various values of E/RT according to each of these approximations with that obtained by numerical quadrature [6]. The various approximations are also shown graphically in Fig. 1. The difference between the value obtained by quadrature and those of the approximations decreases as E/RT increases. However, it is seen that the present approximation, Eq. (7), is the most accurate over the entire range of values of E/RT and is indeed accurate enough for almost all cases.

References

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