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NEW APPROXIMATION FOR THE GENERAL TEMPERATURE INTEGRAL

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A new approximation has been proposed for calculation of the general temperature integral $\int_0^T T^m e^{-E/RT}dT$, which frequently occurs in the nonisothermal kinetic analysis with the dependence of the frequency factor on the temperature ($A=A_0T^m$). It is in the following form:

$$\int_0^T T^m e^{-E/RT}dT=\frac{RT^{m+2}}{E}e^{-E/RT}\frac{0.99954E+(0.044967m+0.58058)RT}{E+(0.94057m+2.5400)RT}$$

The accuracy of the newly proposed approximation is tested by numerical analyses. Compared with other existed approximations for the general temperature integral, the new approximation is significantly more accurate than other approximations.

Keywords: *approximation, integral, non-isothermal kinetics*

Introduction

It has been generally assumed that the reaction rate of thermally stimulated solid-state reactions can be kinetically described by the following expression [1]:

$$\frac{d\alpha}{dt}=Ae^{-E/RT}f(\alpha) \quad (1)$$

where α is the extent of the reaction, t is the time, A is the frequency factor, E is the activation energy, R is the ideal gas constant, T is the absolute temperature, $f(\alpha)$ is the differential conversion function depending on the reaction mechanism.

The most common heating profile for studying solid-state reaction is the linear heating program [2]. For linear heating rate conditions, Eq. (1) can be written

$$\frac{d\alpha}{dT}=\frac{A}{\beta}e^{-E/RT}f(\alpha) \quad (2)$$

where β is the heating rate.

It is noteworthy to point out that all the integral method for the kinetic analysis generally used have been developed by assuming that the frequency factor can be considered as a constant all over the temperature range investigated. However, to some solid-state reactions, the frequency factor is connected with the temperature through the following relationship [3–6]:

$$A=A_0T^m \quad (3)$$

where A_0 is a constant and values of the exponent m range from –1.5 to 2.5 for some solid-state reactions [7].

If Eq. (3) is fulfilled, Eq. (2) becomes:

$$\frac{d\alpha}{dT}=\frac{A_0}{\beta}T^m e^{-E/RT}f(\alpha) \quad (4)$$

Rearranging and integrating Eq. (4) results:

$$g(\alpha)=\int_0^\alpha\frac{d\alpha}{f(\alpha)}=\frac{A}{\beta}\int_0^T T^m e^{-E/RT}dT \quad (5)$$

The integral $\int_0^T T^m e^{-E/RT}dT$ on the right-hand side of Eq. (5) does not have an exact analytical solution. Here we call $\int_0^T T^m e^{-E/RT}dT$ the general temperature integral (when m=0, the integral is usually called the temperature integral [8]). Singh *et al.* developed a technique for the calculation of the integral [9]. However, the technique is complex and takes much computing time. Wanjun *et al.* proposed two approximations for the integral, but the errors in the approximations are large by comparing the resulting values with those calculated by numerical integration [10]. The aim of this work is to present a new approximation for the general temperature integral. It will be shown that the new approximation is very accurate.

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Theory

If E/RT is replaced by 'x' and the integral limits are transformed, the general temperature integral becomes:

$$\int_0^T T^m e^{-E/RT} dT = \left(\frac{E}{R}\right)^{m+1} \int_x^\infty \frac{e^{-x}}{x^{m+2}} dx = \left(\frac{E}{R}\right)^{m+1} p_m(x) \quad (6)$$

An alternative way to express the integral [10] is

$$\int_0^T T^m e^{-E/RT} dT = \frac{RT^{m+2}}{E} e^{-E/RT} h_m(x) \quad (7)$$

If Eqs (6) and (7) are taken into account, the following expression is obtained

$$h_m(x) = x^{m+2} e^x p_m(x) = x^{m+2} e^x \int_x^\infty \frac{e^{-x}}{x^{m+2}} dx \quad (8)$$

The $h_m(x)$ function does not have an exact analytical solution, but can be numerically integrated. In this study, a program developed in Mathematica language has been written for the numerical calculation of the $h_m(x)$ function. Figure 1 illustrates numerical values of $h_m(x)$ as a function of m and x.

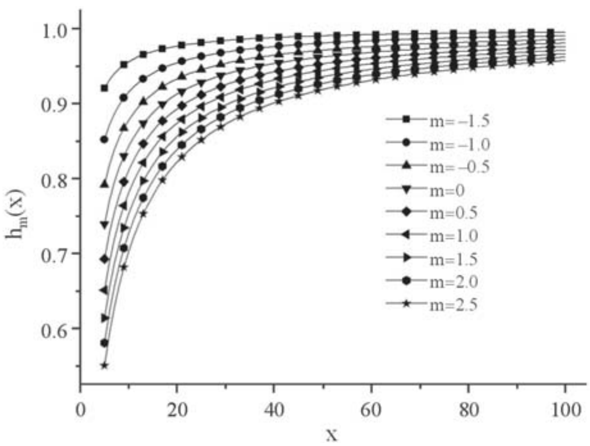

Fig. 1 Numerical values of $h_m(x)$ as a function of m and x

Integrating by part, the $h_m(x)$ function can be expressed as the following series [7]

$$h_m(x) = 1 - \frac{m+2}{x} + \frac{(m+2)(m+3)}{x^2} - \frac{(m+2)(m+3)(m+4)}{x^3} + \ldots \quad (9)$$

From the above formula, we can obtain that the $h_m(x)$ function can be approximated by some rational fractions of x and m. In this work, the following first-degree rational fraction of m and x is used to approximate $h_m(x)$.

$$h_{1m}(x) = \frac{ax + bm + c}{x + dm + e} \quad (10)$$

where $h_{1m}(x)$ is the approximation of $h_m(x)$, a, b, c, d and e are indeterminant parameters.

Based on the numerical results of $h_m(x)$, using a multivariate non-linear regression method performed with the DataFit software, the values of a, b, c, d and e are established: a=0.99954, b=–0.044967, c=0.58058, d=0.94057, e=2.5400. Thus the new approximations for $h_m(x)$ and $p_m(x)$ and the general temperature integral are obtained and given below:

$$h_{1m}(x) = \frac{0.99954x + 0.044967m + 0.58058}{x + 0.94057m + 2.5400} \quad (11)$$

$$p_{1m}(x) = \frac{e^{-x}}{x^{m+2}} \frac{0.99954x + 0.044967m + 0.58058}{x + 0.94057m + 2.5400} \quad (12)$$

$$\int_0^T T^m e^{-E/RT} dT = \frac{RT^{m+2}}{E} e^{-E/RT} \cdot \frac{0.99954E + (0.044967m + 0.58058)RT}{E + (0.94057m + 2.5400)RT} \quad (13)$$

Results and discussion

The aim of this section is to evaluate the accuracy of the newly proposed approximation for the general temperature integral. Since $p_m(x)$ is the variable-transformed expression of the general temperature integral, the accuracy evaluation of the approximation for the general temperature integral is identical to that of the corresponding $p_m(x)$ approximation.

Wanjun *et al.* proposed two approximations for the $p_m(x)$ function [10]:

Wanjun approximation I

$$\frac{e^{-x}}{x^{m+2}\left(1 + \frac{m+2}{x}\right)} \quad (14)$$

Wanjun approximation II

$$\frac{e^{-x}}{x^{m+2}\left[1 + (m+2)\left(0.00099441 + \frac{0.93695599}{x}\right)\right]} \quad (15)$$

Here we have introduced the above two $p_m(x)$ approximations for comparison. The relative error percentages of the newly proposed $p_m(x)$ approximation, Wanjun approximation I and Wanjun approximation II for the estimation of the $p_m(x)$ function are listed in Tables 1–3, respectively. The relative error has been defined by the expression:

$$\varepsilon = \frac{p_{1m}(x) - p_m(x)}{p_m(x)} \cdot 100\% \quad (16)$$

Table 1 Relative error percentages of the newly proposed $p_m(x)$ approximation for the estimation of the $p_m(x)$ function

x	m								
	–1.5	–1.0	-0.5	0.0	0.5	1.0	1.5	2.0	2.5
5	3.7296E-02	–3.5408E-03	8.9099E-03	5.1301E-02	1.0749E-01	1.6633E-01	2.2018E-01	2.6387E-01	2.9400E-01
10	2.8232E-02	1.1503E-03	–1.8658E-02	–3.4021E-02	–4.7160E-02	–5.9819E-02	–7.3361E-02	–8.8845E-02	–1.0709E-01
15	2.0427E-02	1.1742E-02	3.5584E-03	–4.7418E-03	–1.3665E-02	–2.3628E-02	–3.4969E-02	–4.7962E-02	–6.2827E-02
20	1.2292E-02	1.2028E-02	1.0881E-02	8.6837E-03	5.2931E-03	5.9307E-04	–5.5120E-03	–1.3099E-02	–2.2230E-02
25	5.3641E-03	9.0627E-03	1.1637E-02	1.3040E-02	1.3233E-02	1.2183E-02	9.8681E-03	6.2699E-03	1.3761E-03
30	–3.0921E-04	5.3146E-03	9.8590E-03	1.3315E-02	1.5676E-02	1.6939E-02	1.7104E-02	1.6173E-02	1.4149E-02
35	–4.9508E-03	1.5976E-03	7.1795E-03	1.1799E-02	1.5460E-02	1.8171E-02	1.9937E-02	2.0767E-02	2.0669E-02
40	–8.7847E-03	–1.8323E-03	4.2728E-03	9.5388E-03	1.3974E-02	1.7588E-02	2.0388E-02	2.2386E-02	2.3590E-02
45	–1.1990E-02	–4.9157E-03	1.4196E-03	7.0246E-03	1.1908E-02	1.6080E-02	1.9549E-02	2.2323E-02	2.4413E-02
50	–1.4702E-02	–7.6622E-03	–1.2680E-03	4.4888E-03	9.6166E-03	1.4124E-02	1.8019E-02	2.1310E-02	2.4006E-02
55	–1.7024E-02	–1.0104E-02	–3.7523E-03	2.0405E-03	7.2816E-03	1.1979E-02	1.6139E-02	1.9770E-02	2.2879E-02
60	–1.9030E-02	–1.2280E-02	–6.0292E-03	–2.7235E-04	4.9976E-03	9.7874E-03	1.4103E-02	1.7952E-02	2.1340E-02
65	–2.0781E-02	–1.4223E-02	–8.1087E-03	–2.4326E-03	2.8112E-03	7.6287E-03	1.2025E-02	1.6007E-02	1.9579E-02
70	–2.2321E-02	–1.5966E-02	–1.0007E-02	–4.4388E-03	7.4331E-04	5.5445E-03	9.9698E-03	1.4024E-02	1.7712E-02
75	–2.3686E-02	–1.7536E-02	–1.1741E-02	–6.2969E-03	–1.1994E-03	3.5560E-03	7.9737E-03	1.2058E-02	1.5813E-02
80	–2.4903E-02	–1.8955E-02	–1.3328E-02	–8.0165E-03	–3.0179E-03	1.6720E-03	6.0569E-03	1.0141E-02	1.3927E-02
85	–2.5996E-02	–2.0244E-02	–1.4783E-02	–9.6083E-03	–4.7171E-03	–1.0572E-04	4.2290E-03	8.2903E-03	1.2081E-02
90	–2.6982E-02	–2.1419E-02	–1.6121E-02	–1.1083E-02	–6.3038E-03	–1.7792E-03	2.4933E-03	6.5168E-03	1.0294E-02
95	–2.7875E-02	–2.2494E-02	–1.7354E-02	–1.2452E-02	–7.7859E-03	–3.3529E-03	8.4958E-04	4.8241E-03	8.5731E-03
100	–2.8689E-02	–2.3481E-02	–1.8493E-02	–1.3724E-02	–9.1711E-03	–4.8322E-03	–7.0495E-04	3.2130E-03	6.9237E-03

Table 2 Relative error percentages of Wanjun approximation I for the estimation of the $p_m(x)$ function

x	m								
	–1.5	–1.0	-0.5	0.0	0.5	1.0	1.5	2.0	2.5
5	–1.2700E+00	–2.2037E+00	–2.8931E+00	–3.4025E+00	–3.7774E+00	–4.0507E+00	–4.2467E+00	–4.3833E+00	–4.4740E+00
10	–3.8759E-01	–7.1453E-01	–9.9087E-01	–1.2248E+00	–1.4230E+00	–1.5910E+00	–1.7333E+00	–1.8537E+00	–1.9555E+00
15	–1.8600E-01	–3.5121E-01	–4.9813E-01	–6.2890E-01	–7.4540E-01	–8.4925E-01	–9.4184E-01	–1.0244E+00	–1.0981E+00
20	–1.0900E-01	–2.0851E-01	–2.9942E-01	–3.8253E-01	–4.5855E-01	–5.2812E-01	–5.9182E-01	–6.5016E-01	–7.0360E-01
25	–7.1568E-02	–1.3803E-01	–1.9977E-01	–2.5716E-01	–3.1054E-01	–3.6019E-01	–4.0639E-01	–4.4940E-01	–4.8945E-01
30	–5.0578E-02	–9.8094E-02	–1.4275E-01	–1.8474E-01	–2.2422E-01	–2.6137E-01	–2.9633E-01	–3.2923E-01	–3.6021E-01
35	–3.7635E-02	–7.3293E-02	–1.0709E-01	–1.3913E-01	–1.6951E-01	–1.9832E-01	–2.2566E-01	–2.5160E-01	–2.7622E-01
40	–2.9095E-02	–5.6840E-02	–8.3302E-02	–1.0855E-01	–1.3264E-01	–1.5563E-01	–1.7758E-01	–1.9853E-01	–2.1854E-01
45	–2.3164E-02	–4.5366E-02	–6.6648E-02	–8.7053E-02	–1.0662E-01	–1.2539E-01	–1.4339E-01	–1.6066E-01	–1.7723E-01
50	–1.8879E-02	–3.7047E-02	–5.4534E-02	–7.1367E-02	–8.7574E-02	–1.0318E-01	–1.1821E-01	–1.3269E-01	–1.4663E-01
55	–1.5682E-02	–3.0824E-02	–4.5447E-02	–5.9570E-02	–7.3213E-02	–8.6393E-02	–9.9128E-02	–1.1143E-01	–1.2333E-01
60	–1.3233E-02	–2.6047E-02	–3.8456E-02	–5.0475E-02	–6.2117E-02	–7.3395E-02	–8.4322E-02	–9.4909E-02	–1.0517E-01
65	–1.1316E-02	–2.2300E-02	–3.2963E-02	–4.3315E-02	–5.3366E-02	–6.3126E-02	–7.2603E-02	–8.1808E-02	–9.0748E-02
70	–9.7878E-03	–1.9308E-02	–2.8569E-02	–3.7578E-02	–4.6343E-02	–5.4871E-02	–6.3169E-02	–7.1244E-02	–7.9103E-02
75	–8.5494E-03	–1.6880E-02	–2.4998E-02	–3.2909E-02	–4.0620E-02	–4.8136E-02	–5.5462E-02	–6.2603E-02	–6.9565E-02
80	–7.5319E-03	–1.4883E-02	–2.2057E-02	–2.9060E-02	–3.5896E-02	–4.2569E-02	–4.9084E-02	–5.5444E-02	–6.1655E-02
85	–6.6859E-03	–1.3220E-02	–1.9607E-02	–2.5849E-02	–3.1951E-02	–3.7915E-02	–4.3747E-02	–4.9447E-02	–5.5021E-02
90	–5.9749E-03	–1.1821E-02	–1.7543E-02	–2.3142E-02	–2.8622E-02	–3.3985E-02	–3.9235E-02	–4.4373E-02	–4.9403E-02
95	–5.3715E-03	–1.0634E-02	–1.5789E-02	–2.0839E-02	–2.5788E-02	–3.0636E-02	–3.5387E-02	–4.0043E-02	–4.4605E-02
100	–4.8551E-03	–9.6162E-03	–1.4285E-02	–1.8864E-02	–2.3355E-02	–2.7759E-02	–3.2079E-02	–3.6316E-02	–4.0473E-02

Table 3 Relative error percentages of Wanjun approximation II for the estimation of the $p_m(x)$ function

x	m								
	–1.5	–1.0	-0.5	0.0	0.5	1.0	1.5	2.0	2.5
5	–7.4604E-01	–1.2479E+00	–1.5741E+00	–1.7727E+00	–1.8781E+00	–1.9147E+00	–1.9009E+00	–1.8500E+00	–1.7720E+00
10	–1.3507E-01	–2.3292E-01	–3.0035E-01	–3.4284E-01	–3.6488E-01	–3.7014E-01	–3.6161E-01	–3.4178E-01	–3.1270E-01
15	–3.0794E-02	–5.0562E-02	–6.0867E-02	–6.3049E-02	–5.8262E-02	–4.7495E-02	–3.1605E-02	–1.1331E-02	1.2688E-02
20	–3.7472E-03	–3.0122E-03	1.6722E-03	9.8349E-03	2.1059E-02	3.4975E-02	5.1254E-02	6.9606E-02	8.9771E-02
25	3.3045E-03	8.8474E-03	1.6399E-02	2.5751E-02	3.6716E-02	4.9125E-02	6.2826E-02	7.7679E-02	9.3558E-02
30	3.8700E-03	9.0504E-03	1.5424E-02	2.2883E-02	3.1331E-02	4.0675E-02	5.0835E-02	6.1734E-02	7.3302E-02
35	2.1398E-03	5.1542E-03	8.9757E-03	1.3542E-02	1.8794E-02	2.4679E-02	3.1147E-02	3.8151E-02	4.5649E-02
40	–3.6964E-04	–8.9283E-05	7.9801E-04	2.2520E-03	4.2350E-03	6.7117E-03	9.6493E-03	1.3017E-02	1.6785E-02
45	–3.0600E-03	–5.5950E-03	–7.6346E-03	–9.2069E-03	–1.0338E-02	–1.1053E-02	–1.1376E-02	–1.1328E-02	–1.0930E-02
50	–5.6880E-03	–1.0925E-02	–1.5733E-02	–2.0133E-02	–2.4144E-02	–2.7785E-02	–3.1074E-02	–3.4027E-02	–3.6660E-02
55	–8.1584E-03	–1.5913E-02	–2.3280E-02	–3.0276E-02	–3.6916E-02	–4.3215E-02	–4.9187E-02	–5.4844E-02	–6.0201E-02
60	–1.0440E-02	–2.0508E-02	–3.0216E-02	–3.9578E-02	–4.8606E-02	–5.7312E-02	–6.5708E-02	–7.3804E-02	–8.1610E-02
65	–1.2532E-02	–2.4713E-02	–3.6554E-02	–4.8067E-02	–5.9261E-02	–7.0147E-02	–8.0734E-02	–9.1032E-02	–1.0105E-01
70	–1.4443E-02	–2.8551E-02	–4.2335E-02	–5.5803E-02	–6.8964E-02	–8.1827E-02	–9.4400E-02	–1.0669E-01	–1.1871E-01
75	–1.6188E-02	–3.2055E-02	–4.7608E-02	–6.2856E-02	–7.7806E-02	–9.2467E-02	–1.0684E-01	–1.2095E-01	–1.3478E-01
80	–1.7784E-02	–3.5257E-02	–5.2426E-02	–6.9298E-02	–8.5880E-02	–1.0218E-01	–1.1820E-01	–1.3395E-01	–1.4944E-01
85	–1.9245E-02	–3.8188E-02	–5.6835E-02	–7.5193E-02	–9.3267E-02	–1.1106E-01	–1.2859E-01	–1.4585E-01	–1.6285E-01
90	–2.0587E-02	–4.0879E-02	–6.0882E-02	–8.0602E-02	–1.0004E-01	–1.1922E-01	–1.3812E-01	–1.5676E-01	–1.7515E-01
95	–2.1821E-02	–4.3354E-02	–6.4604E-02	–8.5578E-02	–1.0628E-01	–1.2671E-01	–1.4689E-01	–1.6680E-01	–1.8646E-01
100	–2.2959E-02	–4.5636E-02	–6.8037E-02	–9.0166E-02	–1.1203E-01	–1.3363E-01	–1.5497E-01	–1.7606E-01	–1.9690E-01

being $p_{1m}(x)$ the value obtained by the $p_m(x)$ approximation and $p_m(x)$ the value obtained by numerical integration which is performed by means of the Mathematica software system.

From Tables 1–3, it is obviously seen that the accuracy of the newly proposed approximation is the highest, and that of Wanjun approximation I is the lowest.

Conclusions

In the present paper we have developed a new approximation for the integral $\int_0^T T^m e^{-E/RT} dT$, which frequently occurs in the nonisothermal kinetic analysis with the dependence of the frequency factor on the temperature ($A=A_0T^m$). The accuracy of the new approximation is tested by numerical analyses. Compared with Wanjun approximations for the integral, the newly proposed approximation is significantly more accurate.

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