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SOME PROBLEMS CONCERNING THE TEMPERATURE INTEGRAL IN NON-ISOTHERMAL KINETICS
Part I. GENERALITIES AND SOME SIMPLE APPLICATIONS

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ABSTRACT

A method to obtain high precision solutions of the temperature integral is presented. Most of the approximation functions are rational. The approximations are competitive with others given in the literature.

INTRODUCTION

In order to describe kinetically reactions which occur in non-isothermal conditions, the classical equation is used [1,2]

$$\frac{\mathrm{d}\alpha}{\mathrm{d}T} = \frac{A}{\beta} f(\alpha)\, \mathrm{e}^{-E/RT} \tag{1}$$

with

$$f(\alpha) = (1-\alpha)^n \alpha^m [-\ln(1-\alpha)]^p \tag{2}$$

and the "classical" conditions

$$A = \text{constant} \tag{3}$$

$$E = \text{constant} \tag{4}$$

$$n = \text{constant}, \quad m = \text{constant}, \quad p = \text{constant} \tag{5}$$

In eqn. (1) and relationships (2)–(5) the parameters have their usual meaning.

The classical case can be generalized for a pre-exponential factor which depends on temperature, i.e.

$$A = A_r T^r \qquad (A_r = \text{constant},\ r = \text{constant}) \tag{6}$$

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Equation (1) with the pre-exponential factor given by eqn. (6) becomes

$$\frac{\mathrm{d}\alpha}{\mathrm{d}T}=\frac{A_r}{\beta}T^r f(\alpha)\,\mathrm{e}^{-E/RT} \tag{7}$$

(The use of a temperature-dependent pre-exponential factor does not violate the classical conditions. As shown in our previous paper [1] non-classical conditions indicate dependence of the kinetic parameters on conversion.) Equations of the form (1) and (7) can be obtained from the isothermal differential kinetic equation

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t}=A_r T^r f(\alpha)\,\mathrm{e}^{-E/RT} \qquad (T=\text{constant}) \tag{8}$$

(considered as the postulated primary isothermal differential kinetic equation (P-PIDKE) [3–5]) by applying the classical non-isothermal change [3–5], the temperature being given by

$$T=T_0+\beta t \qquad (\beta=\text{constant}) \tag{9}$$

The following considerations are valid for a constant heating rate.

Equation (7) through variable separations and subsequent integration leads successively to

$$\frac{\mathrm{d}\alpha}{f(\alpha)}=\frac{A_r}{\beta}T^r\,\mathrm{e}^{-E/RT}\,\mathrm{d}T \tag{10}$$

$$\int_{\alpha_1}^{\alpha_2}\frac{\mathrm{d}\alpha}{f(\alpha)}=\frac{A_r}{\beta}\int_{T_1}^{T_2}y^r\,\mathrm{e}^{-E/Ry}\,\mathrm{d}y \tag{11}$$

The integral from the right-hand side of eqn. (11) can be written as

$$\int_{T_1}^{T_2}y^r\,\mathrm{e}^{-E/Ry}\,\mathrm{d}y=\int_0^{T_2}y^r\,\mathrm{e}^{-E/Ry}\,\mathrm{d}y-\int_0^{T_1}y^r\,\mathrm{e}^{-E/Ry}\,\mathrm{d}y \tag{12}$$

Thus to solve the integral from the right-hand side of eqn. (11) we must solve the integrals of the form $\int_0^T y^r\,\mathrm{e}^{-E/Ry}\,\mathrm{d}y$, which are frequently met in non-isothermal kinetics [6] and are called temperature integrals.

THEORETICAL ASPECTS CONCERNING THE APPROXIMATE SOLUTION OF THE TEMPERATURE INTEGRAL

In the literature, two techniques have been employed to solve the temperature integral approximately: (a) the use of series for approximation [6–14] and (b) the use of approximate formulae for the temperature integral. Case (b) is discussed here. It should be emphasized that the temperature integral cannot be solved exactly.

To obtain an approximate solution of the temperature integral, let us suppose that

$$\int_0^T y^r\,\mathrm{e}^{-E/Ry}\,\mathrm{d}y=\frac{R}{E}T^{r+2}\,\mathrm{e}^{-E/RT}Q_r\left(\frac{E}{RT}\right) \tag{13}$$

Taking the derivative of eqn. (13) with respect to T we obtain

$$T^r \mathrm{e}^{-E/RT} = (r+2)\frac{R}{E} T^{r+1} \mathrm{e}^{-E/RT} Q_r\left(\frac{E}{RT}\right) + T^r \mathrm{e}^{-E/RT} Q_r\left(\frac{E}{RT}\right) - T^r \mathrm{e}^{-E/RT} Q_r'\left(\frac{E}{RT}\right) \tag{14}$$

where $Q_r'(E/RT)$ is the derivative with respect to the variable E/RT. From eqn. (14), after performing the calculations, we obtain

$$Q_r'\left(\frac{E}{RT}\right) - \left(1 + \frac{r+2}{E/RT}\right) Q_r\left(\frac{E}{RT}\right) + 1 = 0 \tag{15}$$

Equation (15) with the notation

$$x = \frac{E}{RT} > 0 \tag{16}$$

becomes

$$Q_r'(x) - \left(1 + \frac{r+2}{x}\right) Q_r(x) + 1 = 0 \qquad (r \geq 0) \tag{17}$$

The differential equation (17) does not have an exact solution and from the information standpoint is equivalent to approximation (13). Thus to solve the temperature integral approximately we must find an approximate solution for differential equation (17) where

$$0 < Q_r(x) < 1 \tag{18}$$

We propose a solution of the form

$$Q(x,\ p(x),\ c_i) \tag{19}$$

with

$$i = 1, 2, \ldots, N \tag{20}$$

where $p(x)$ is a parameter which depends on x and changes smoothly with it and $c_1, c_2, \ldots, c_N$ are constants.

To approximate $p(x)$ we must introduce eqn. (19) into eqn. (17). We obtain

$$\frac{\partial Q_r(x,\ p(x),\ c_i)}{\partial x} + \frac{\partial Q_r(x,\ p(x),\ c_i)}{\partial p(x)} \frac{\mathrm{d}p(x)}{\mathrm{d}x} - \left(1 + \frac{r+2}{x}\right) Q_r(x,\ p(x),\ c_i) + 1 = 0 \tag{21}$$

A first approximation for $p(x)$, $p_0(x,\ c_i)$, corresponds to the case for which the term

$$\frac{\partial Q_r(x,\ p_0(x,\ c_i) c_i)}{\partial p_0(x,\ c_i)} \frac{\mathrm{d}p_0(x,\ c_i)}{\mathrm{d}x} \tag{22}$$

can be neglected in eqn. (21). In such conditions

$$\frac{\partial Q_r(x,\ p_0(x,\ c_i)c_i)}{\partial x} - \left(1 + \frac{r+2}{x}\right)Q_r(x,\ p_0(x,\ c_i)c_i) + 1 = 0 \tag{23}$$

Taking into account this result, $p_0(x,\ c_i)$ is obtained as the solution of an algebraic equation. Introducing $p_0(x,\ c_i)$ into eqn. (19), the approximation

$$Q_r(x,\ p_0(x,\ c_i),\ c_i) \tag{24}$$

is obtained.

The procedures to determine the constants $c_1,\ c_2, \ldots,\ c_N$ are given below. In some simple cases, function (19) should not contain the constants c_i.

APPLICATIONS

In this section, some applications of eqn. (23) and the corresponding particular forms of function (24) for five values of r (0, $\frac{1}{2}$, 1, $\frac{3}{2}$ and 2) are presented. The approximations are checked by calculating the value of $Q_r(x)$ for values of x of 5, 10, 20, 30, 40, 50, 75 and 100 and determining relative percentage error with respect to numerically evaluated $Q_r(x)$ values. The $Q_r(x)$ values obtained via numeric procedures using relationship (13) are given in Table 1.

As the $Q_r(x)$ values in Table 1 are given with a precision of $\pm 2 \times 10^{-7}$ and the $Q_r(x)$ values calculated for various approximations are compared with those in Table 1, a relative error lower than $(2 \times 10^{-7}/Q_r(x)) \times 100$ is not significant. Values of the relative percentage error ϵ_r which do not fulfil the condition

$$|\epsilon_r| \geqslant \frac{2 \times 10^{-5}}{Q_r(x)} \tag{25}$$

are given by $\approx 10^{-5}$ or $\approx -10^{-5}$.

TABLE 1

Values of the function $Q_r(x)$ for various values of x and r [a]

Number	x	$Q(x)$	$Q_{1/2}(x)$	$Q_1(x)$	$Q_{3/2}(x)$	$Q_2(x)$
1	5	0.7394456	0.6928382	0.6513860	0.6143237	0.5810234
2	10	0.8436667	0.8115484	0.7816671	0.7538065	0.7277768
3	20	0.9125819	0.8929838	0.8741822	0.8561305	0.8387868
4	30	0.9392349	0.9251512	0.9114731	0.8981838	0.8852674
5	40	0.9534159	0.9424266	0.9316828	0.9211763	0.9108997
6	50	0.9622251	0.9532157	0.9443707	0.9356855	0.9271562
7	75	0.9743459	0.9681345	0.9620008	0.9559435	0.9499611
8	100	0.9805772	0.9758379	0.9711437	0.9664938	0.9618880

[a] Values are given with a precision of $\pm 2 \times 10^{-7}$.

TABLE 2

Coefficients a_i in relationship (26) [15]

r	a_1	a_2	a_3	a_4
0	-2.0	4.0	-10.0	30.0
$\frac{1}{2}$	-2.5	6.25	-18.125	61.563
1	-3.0	9.0	-30.0	114.0
$\frac{3}{2}$	-3.5	12.25	-46.375	190.985
2	-4.0	16.0	-68.0	314.0

Table 2 contains the coefficients a for the following form of $Q_r(x)$ [15]

$$Q_r(x) = 1 + \frac{a_1}{x+1} + \frac{a_2}{(x+1)(x+2)} + \frac{a_3}{(x+1)(x+2)(x+3)} + \frac{a_4}{(x+1)(x+2)(x+3)(x+4)} \tag{26}$$

which is used for comparison. In Table 3 some functions $Q(x)$ ($r=0$) taken from the literature are also given for comparison. Table 4 contains our approximations $Q(x)$ ($r=0$) and Tables 5–8 contain our approximations $Q_r(x)$ ($r=\frac{1}{2}, 1, \frac{3}{2}, 2$) in comparison with $Q_r(x)$ given by eqn. (26).

In the following we describe the new approximations proposed in this work.

Case 1

$$Q_r(x, p(x), c_i) = 1 + \frac{a(x)}{x} \tag{27}$$

$$p(x) = a(x) \tag{27a}$$

The particular form of eqn. (23) is

$$-\frac{a_0(x)}{x^2} - \left(1 + \frac{r+2}{x}\right)\left(1 + \frac{a_0(x)}{x}\right) + 1 = 0 \tag{28}$$

From eqn. (28) we obtain

$$a_0(x) = -\frac{(r+2)x}{x+r+3} \tag{29}$$

Thus

$$Q_r(x) \approx \frac{x+1}{x+r+3} \tag{30}$$

or

$$Q_r(x) \approx 1 - \frac{r+2}{x+r+3} \tag{31}$$

TABLE 3

$Q(x)$ ($r = 0$) approximations taken from the literature

Approximation	$Q(x)$ ($r=0$)	Degree [a]	Reference	x = 5	x = 10
1	1	0	[16–19,25]	35.23	18.53
2	$\frac{x-2}{x}$	1	[8,11,16–21,25]	−18.86	−5.18
3	$\frac{x}{x+2}$	1	[8,11,18,19,21,22,25]	−3.40	−1.22
4	$\frac{x+1}{x+3}$	1	[23], this work (eqn. (32))	1.43	0.295
5	$\frac{1}{(1+4/x)^{1/2}}$	–	[11,19,25]	0.799	0.176
6	$\frac{x^2-2x}{x^2-6}$	2	[18,24,25]	6.77	0.877
7	$\frac{x^2-2x}{x^2-5}$	2	[18,25]	1.43	−0 185
8	$\frac{0.995924x^2+1\,430913x}{x^2+3\,330657x+1.681534}$	2	[21,25]	−0.028	−0.015
9	$\frac{x^2+4x}{x^2+6x+6}$	2	[8,21,25]	−0.235	−0.035
10	$\frac{x^3+10x^2+18x}{x^3+12x^2+36x+24}$	3	[8,21,25]	−0.024	−0.0016
11	$\frac{x^4+18x^3+88x^2+96x}{x^4+20x^3+120x^2+240x+120}$	4	[21,26–28]	0.905	0.532
12	$\frac{x^4-4x^3+84x^2}{(x+2)(x^3-4x^2+84x-16)}$	4	[8,25,29]	0.200	−0.115
13	$\frac{x^4+6\,055x^3-57.412x^2-674\,567x}{x^4+8.02x^3-49.313x^2-841.655x-1699.066}$	4	[8,30]	–	–
14	$1+\frac{a_1}{x+1}+\frac{a_2}{(x+1)(x+2)}+\ldots+\frac{a_4}{(x+1)(x+2)(x+3)(x+4)}$	4	[15], this work (Table 2)	0.354	0.028

[a] The degrees of the polynomials from the numerator and denominator of the fraction are given.

For the most important case with $r = 0$,

$$Q(x) \approx \frac{x+1}{x+3} \tag{32}$$

Case 2

$$Q_r(x,\ p(x),\ c_i) = 1 + \frac{a(x)}{x+b} \tag{33}$$

$$p(x) = a(x),\ i = 1,\ c_1 = b \tag{34}$$

20	30	40	50	75	100
9.58	6.47	4.89	3.93	2.63	1.98
−1.38	−0.628	−0.358	−0.231	−0.104	−0.059
−0.383	−0.185	−0.109	−0.071	−0.033	−0.019
0.051	0.017	0.008	0.004	0.001	5×10^{-4}
0.032	0.011	0.005	0.003	9×10^{-4}	4×10^{-4}
0.123	0.039	0.017	0.009	0.003	0.001
−0.130	−0.073	−0.046	−0.031	−0.015	−0.009
−0.086	−0.157	−0.204	−0.236	−0.285	−0.312
−0.004	-8.9×10^{-4}	-3.3×10^{-4}	-1.4×10^{-4}	-4×10^{-5}	-2×10^{-5}
-7.6×10^{-5}	$\approx 2\times 10^{-5}$	$\approx -10^{-5}$	$\approx 10^{-5}$	$\approx -10^{-5}$	$\approx -10^{-5}$
0.235	0.131	0.083	0.057	0.028	0.017
−0.185	−0.123	−0.082	−0.058	−0.029	−0.017
1.375	0.492	0.266	0.174	0.087	0.056
0.002	2.9×10^{-4}	7.3×10^{-5}	3.1×10^{-5}	$\approx 10^{-5}$	$\approx -10^{-5}$

For this case, eqn. (23) takes the form

$$\frac{a_0(x)}{(x+b)^2} - \left(1+\frac{r+2}{x}\right)\left(1+\frac{a_0(x)}{x+b}\right) + 1 = 0 \qquad (35)$$

whose solution is

$$a_0(x) = -\frac{(r+2)(x+b)^2}{[x+(x+b)(x+r+2)]} \qquad (36)$$

From eqns. (33) and (36) we obtain

$$Q_r(x,\ b) \approx \frac{x^2+x(b+1)}{x^2+x(b+r+3)+b(r+2)} \qquad (37)$$

TABLE 4

Approximations $Q(x)$ proposed in this work ($r = 0$)

Approx-imation	$Q(x)(r=0)$	Deg-ree	Equation	x: 5	10	20	30	40	50	75	100
1	$\frac{x^2+2x-2}{x^2+4x}$	2	Eqn. (50), $r=0$	$-0\ 827$	-0.096	-0.009	-0.002	-7.1×10^{-4}	-3.0×10^{-4}	$\approx10^{-5}$	-2.86×10^{-5}
2	$\frac{x^2+3.5x}{x^2+5.5x+5}$	2	Eqn. (56)	-0.043	0.010	0 004	0.002	9.2×10^{-4}	$5\ 3\times10^{-4}$	2.5×10^{-4}	7.3×10^{-5}
3	$\frac{x^2+5\ 347x+1.376}{x^2+7\ 347x+10.069}$	2	Eqn. (62)	0.030	1.7×10^{-4}	$-6\ 6\times10^{-5}$	$6\ 3\times10^{-5}$	4.1×10^{-5}	$4\ 4\times10^{-5}$	9.3×10^{-5}	$\approx10^{-5}$
4	$2+\frac{2}{x}-\left(1+\frac{8}{x}+\frac{4}{x^2}\right)^{1/2}$	–	Eqn. (46), $r=0$	-0.104	-0.016	$-0\ 002$	-4.1×10^{-4}	-1.6×10^{-4}	-5.2×10^{-5}	7.2×10^{-5}	$\approx10^{-5}$

TABLE 5

Approximations $Q_{1/2}(x)$ proposed in this work

Approximation	$Q_{1/2}(x)$ $(r=1/2)$	Degree	Source	x = 5	10	20	30	40	50	75	100
1	$\frac{x+1}{x+3.5}$	1	Eqn. (30), $r=\frac{1}{2}$	1.883	0.402	0.071	0.024	0.011	0.006	0.002	7.7×10^{-4}
2	$\frac{x^2+4x}{x^2+6.5x+7.5}$	2	Eqn. (39), $r=\frac{1}{2}$	−0.077	0.006	0.004	0.002	0.001	6.1×10^{-4}	2.8×10^{-4}	7.3×10^{-5}
3	$\frac{x^2+4.5x}{x^2+7x+8.75}$	2	Eqn. (41), $r=\frac{1}{2}$	−0.278	−0.044	−0.005	−0.001	-4.6×10^{-4}	-2.0×10^{-4}	2.7×10^{-5}	-4.0×10^{-5}
4	$\frac{x^2+2x-2.50}{x^2+4.5x}$	2	Eqn. (50), $r=\frac{1}{2}$	−1.245	−0.148	−0.014	−0.003	−0.001	-4.9×10^{-4}	-3.4×10^{-5}	-5.9×10^{-5}
5	$1+1.25\left[1+\frac{2.5}{x}-\left(1+\frac{9}{x}+\frac{6.25}{x^2}\right)^{1/2}\right]$	-	Eqn. (46), $r=\frac{1}{2}$	−0.126	−0.020	−0.002	-5.7×10^{-4}	-2.2×10^{-4}	-8.4×10^{-5}	5.2×10^{-5}	-3.1×10^{-5}
6	$1+\frac{a_1}{(x+1)}+\dots+\frac{a_4}{(x+1)(x+2)(x+3)(x+4)}$	4	Eqn. (26), [15]	0.826	0.065	0.004	6.2×10^{-4}	1.5×10^{-4}	6.3×10^{-5}	8.3×10^{-5}	-2.1×10^{-5}

TABLE 6

Approximations $Q_1(x)$ proposed in this work

Approximation	$Q_1(x)\,(r=1)$	Degree	Source	x = 5	10	20	30	40	50	75	100
1	$\frac{x+1}{x+4}$	1	Eqn (30), $r=1$	2.346	0.518	0.094	0.032	0.015	0.008	0.003	0.001
2	$\frac{x^2+4x}{x^2+7x+9}$	2	Eqn. (39), $r=1$	0.121	0.058	0.015	0.006	0.003	0.002	6.3×10^{-4}	2.1×10^{-4}
3	$\frac{x^2+5x}{x^2+8x+12}$	2	Eqn. (41), $r=1$	−0.313	−0.053	−0.006	−0.002	-6.2×10^{-4}	-2.7×10^{-4}	$\approx10^{-5}$	-5.5×10^{-5}
4	$\frac{x^2+2x-3}{x^2+5x}$	2	Eqn. (50), $r=1$	−1.748	−0.213	−0.021	−0.005	−0.002	-7.5×10^{-4}	-8.3×10^{-5}	-8.8×10^{-5}
5	$2.5+\frac{4.5}{x}-1.5\left(1+\frac{10}{x}+\frac{9}{x^2}\right)^{1/2}$	-	Eqn. (46), $r=1$	−0.143	−0.025	−0.003	-7.5×10^{-4}	-3.0×10^{-4}	-1.27×10^{-4}	6.2×10^{-5}	-4.1×10^{-5}
6	$1+\frac{a_1}{(x+1)}+\ldots+\frac{a_4}{(x+1)(x+2)(x+3)(x+4)}$	4	Eqn. (26), [15]	1.737	0.134	0.007	0.001	3.0×10^{-4}	1.1×10^{-4}	9.4×10^{-5}	3.1×10^{-5}

TABLE 7

Approximations $Q_{3/2}(x)$ proposed in this work

Approximation	$Q_{3/2}(x)$ $(r=3/2)$	Degree	Source	x = 5	10	20	30	40	50	75	100
1	$\dfrac{x+1}{x+4.5}$	1	Eqn. (30), $r=\frac{3}{2}$	2.809	0.639	0.118	0.041	0.019	0.010	0.003	0.001
2	$\dfrac{x^2+4x}{x^2+7.5x+10.5}$	2	Eqn (39), $r=\frac{3}{2}$	0.344	0.121	0.029	0.011	0.005	0.003	0.001	4.2×10^{-4}
3	$\dfrac{x^2+5.5x}{x^2+9x+15.75}$	2	Eqn. (41), $r=\frac{3}{2}$	−0.338	−0.062	−0.008	−0.002	-7.7×10^{-4}	-3.4×10^{-4}	$\approx10^{-5}$	-4.6×10^{-5}
4	$\dfrac{x^2+2x-3.5}{x^2+5.5x}$	2	Eqn (50), $r=\frac{3}{2}$	−2.332	−0.291	−0.029	−0.007	−0.002	−0.001	1.6×10^{-4}	-9.4×10^{-5}
5	$2.75+\dfrac{6.125}{x}-1.75\left(1+\dfrac{11}{x}+\dfrac{12.25}{x^2}\right)^{1/2}$	-	Eqn. (46), $r=\frac{3}{2}$	−0.157	−0.029	−0.004	-9.4×10^{-4}	-3.7×10^{-4}	-1.6×10^{-4}	6.3×10^{-5}	$\approx10^{-5}$
6	$1+\dfrac{a_1}{x+1}+\ldots+\dfrac{a_4}{(x+1)(x+2)(x+3)(x+4)}$	4	Eqn. (26), [15]	3.117	0.231	0.012	0.002	4.3×10^{-4}	1.5×10^{-4}	9.4×10^{-5}	$\approx-10^{-5}$

TABLE 8

Approximations $Q_2(x)$ proposed in this work

Approximation	$Q_2(x)$ ($r=2$)	Degree	Source	x = 5	10	20	30	40	50	75	100
1	$\frac{x+1}{x+5}$	1	Eqn (30), $r=2$	3.266	0.764	0.145	0.051	0.023	0.013	0.004	0.002
2	$\frac{x^2+4x}{x^2+8x+12}$	2	Eqn. (39), $r=2$	0.584	0.191	0.045	0.017	0.008	0.004	0.002	6.4×10^{-4}
3	$\frac{x^2+6x}{x^2+10x+20}$	2	Eqn. (41), $r=2$	−0.357	−0.069	−0.009	−0.002	-9.5×10^{-4}	-4.2×10^{-4}	-2.1×10^{-5}	-5.5×10^{-5}
4	$\frac{x^2+2x-4}{x^2+6x}$	2	Eqn. (50), $r=2$	−2.993	−0.382	−0.039	−0.009	−0.003	−0.001	-2.4×10^{-4}	-1.3×10^{-4}
5	$3+\frac{8}{x}-2\left(1+\frac{12}{x}+\frac{16}{x^2}\right)^{1/2}$	–	Eqn.(46), $r=2$	−0.167	−0.0323	−0.004	−0.001	-4.7×10^{-4}	-1.9×10^{-4}	4.2×10^{-5}	-2.1×10^{-5}
6	$1+\frac{a_1}{x+1}+\dots+\frac{a_4}{(x+1)(x+2)(x+3)(x+4)}$	4	Eqn. (26), [15]	5.975	0.446	0.021	0.004	9.8×10^{-3}	3.5×10^{-4}	1.3×10^{-4}	$\approx-10^{-5}$

For

$$b = 3 \tag{38}$$

$$Q_r(x) \approx \frac{x^2 + 4x}{x^2 + x(6 + r) + 3(r + 2)} \tag{39}$$

Approximation (39) leads to satisfactory results. Nevertheless, as eqn. (33) is suggested by a relationship of the form of eqn. (31) we propose

$$b = 3 + r \tag{40}$$

Thus from eqn. (37)

$$Q_r(x) \approx \frac{x^2 + x(4 + r)}{x^2 + x(6 + 2r) + (r + 3)(r + 2)} \tag{41}$$

For $r = 0$, approximations (39) and (41) lead to

$$Q(x) \approx \frac{x^2 + 4x}{x^2 + 6x + 6} \tag{42}$$

which is well known in the literature [8,21,25].

Case 3

$$Q_r(x, p(x), c_i) = 1 + \frac{a}{x + b(x)} \tag{43}$$

$$p(x) = b(x), \; i = 1, \; c_1 = a$$

By writing the particular form of eqn. (23), solving it with respect to $b(x)$ and introducing the result into eqn. (43) we obtain

$$Q_r(x, a) \approx \frac{2 - a}{2} - \frac{a(r + 2)}{2x} - \left[\frac{a^2}{4} + \frac{a(a - 2)(r + 2)}{2x} + \frac{a^2(r + 2)^2}{4x^2}\right]^{1/2} \tag{44}$$

As eqn. (43) is suggested by a relationship of the form of eqn. (31), we propose

$$a \approx -(r + 2) \tag{45}$$

In this case relationship (44) becomes

$$Q_r(x) \approx 1 + \frac{r + 2}{2}\left\{1 + \frac{r + 2}{x} - \left[1 + \frac{2(r + 4)}{x} + \frac{(r + 2)^2}{x^2}\right]^{1/2}\right\} \tag{46}$$

The results obtained using eqn. (46) are given in Tables 4–8.

Case 4

$$Q_r(x, p(x), c_i) = 1 + \frac{a}{x} + \frac{b(x)}{x^2} \tag{47}$$

Applying the usual procedure we obtain

$$Q_r(x, a) \approx \frac{x^2 + 2x + a}{x^2 + (r+4)x} \tag{48}$$

$$a = -(r+2) \tag{49}$$

$$Q_r(x) \approx \frac{x^2 + 2x - (r+2)}{x^2 + (r+4)x} \tag{50}$$

The results obtained using eqn. (50) are given in Tables 4–8.

The following cases with a more complicated procedure are presented for $r = 0$.

Case 5

Let us suppose that for $r = 0$

$$Q(x, p(x)) \approx \frac{x + p(x)}{x + p(x) + 2} \tag{51}$$

Using the values of $Q(x)$ given in Table 1 in eqn. (51)

$$\frac{x + p(x)}{x + p(x) + 2} = Q(x) \tag{52}$$

and solving this equation with respect to $p(x)$, we obtain

$$p(x) = \frac{2Q(x)}{1 - Q(x)} - x \tag{53}$$

In this way, the values of $p(x)$ can be estimated for the eight values of x given in Table 1. Using the least-squares method [31,32], an approximation of the form

$$p(x) \approx \frac{c_1 x}{x + c_2} \tag{54}$$

$c_1 = \text{constant}, \ c_2 = \text{constant}$

was employed. After performing the calculations, we obtain

$$p(x) \approx \frac{x}{x + 2.5} \tag{55}$$

and thus

$$Q(x) \approx \frac{x^2 + 3.5x}{x^2 + 5.5x + 5} \tag{56}$$

The results obtained using eqn. (56) are given in Table 4.

Case 6

Considering that $b = b(x)$ in eqn. (37), we obtain

$$Q(x, b(x)) \approx \frac{x^2 + x(b(x) + 1)}{x^2 + x(b(x) + 3) + 2b(x)} \tag{57}$$

Using the eight values of $Q(x)$ given in Table 1 and solving an equation of the form

$$\frac{x^2 + x(b(x) + 1)}{x^2 + x(b(x) + 3) + 2b(x)} = Q(x) \tag{58}$$

with respect to $b(x)$, we obtain

$$b(x) = \frac{(x^2 + x)(1 - Q(x)) - 2xQ(x)}{-x(1 - Q(x)) + 2Q(x)} \tag{59}$$

For instance, if $x = 10$, $b(10) = 2.6075$.

An approximation of the form

$$b(x) \approx \frac{c_1 x}{x + c_2} \tag{60}$$

was employed. Using the least-squares method, we obtain

$$b(x) \approx \frac{2.9712x}{x + 1.3757} \tag{61}$$

Introducing this result in eqn. (57) leads to the following approximation for $Q(x)$

$$Q(x) \approx \frac{x^2 + 5.347x + 1.376}{x^2 + 7.347x + 10.069} \tag{62}$$

The good results obtained using approximation (62) are given in Table 4.

DISCUSSION

The rational approximations for $Q(x)$ given in this work are of the form

$$Q_r(x) = \frac{q_1(x)}{q_2(x)} \tag{63}$$

where $q_1(x)$ and $q_2(x)$ are polynomials of the same degree. The degree of the polynomials gives the degree of the rational approximation for $Q_r(x)$. The higher the degree of the rational approximation, the more complicated $Q_r(x)$ becomes and thus the calculations increase in complexity.

In addition to the rational approximations, relationships such as eqn. (46) or number 5 in Table 3 are proposed. Special emphasis is given to the approximate functions $Q(x)$ ($r = 0$).

From the data given in Tables 3 and 4, we can make the following observations:

(1) the best rational approximation of the first degree is approximation 4 in Table 3;

(2) the best rational approximation of the second degree is approximation 3 in Table 4;

(3) the best approximation is approximation 10 in Table 3 followed by approximation 3 in Table 4;

(4) approximation 9 in Table 4 is very simple and gives good results;

(5) approximation 4 in Table 4 also gives good results;

(6) approximations 11, 12 and 13 in Table 3 do not give as good results as approximations 10 in Table 3 and 3 in Table 4;

(7) although approximation 14 in Table 3 gives good results for $x > 20$, it is not recommended due to its rather complicated form.

For approximations $Q(x)$ with $r \neq 0$, the data given in Tables 5–8 show that number 1 for the first degree, number 3 for the second degree and number 5 from the irrational approximations give the best results. Although approximation 6 gives good results for $x > 20$, it is difficult to handle.

The approximations given by eqns. (30), (39), (41), (46) and (50) can be applied, in principle, for any value of r.

Using the procedures presented here, other approximations can be derived for $Q(x)$.

CONCLUSIONS

(1) It has been shown that the approximate evaluation of the temperature integral consists of finding a solution for the differential equation (17). For such equations, solutions of the form (24) obtained from eqn. (23) are proposed.

(2) A method for the determination of the coefficients c_i is given (see cases 5 and 6).

(3) The precision of the approximations decreases with an increase in r.

(4) The method presented in this work allows us to obtain other approximations by a convenient choice of functions of the form (19).

(5) We recommend the following approximations from this work

$$\int_0^T y^r \, e^{-E/Ry} \, dy \approx \frac{R}{E} T^{r+2} \, e^{-E/RT} \frac{x^2 + x(4+r)}{x^2 + x(6+2r) + (r+3)(r+2)} \tag{64}$$

$$\int_0^T y^r \, e^{-E/Ry} \, dy \approx \frac{R}{E} T^{r+2} \, e^{-E/RT} \frac{x+1}{x+3+r} \tag{65}$$

$$\int_0^T y^r e^{-E/Ry} \, dy \approx \frac{R}{E} T^{r+2}$$

$$\times e^{-E/RT} \left\{ 1 + \frac{r+2}{2} \left[1 + \frac{r+2}{x} - \left(1 + \frac{2(r+4)}{x} + \frac{(r+2)^2}{x^2} \right)^{1/2} \right] \right\} \tag{66}$$

and for $r = 0$

$$\int_0^T e^{-E/Ry} \, dy \approx \frac{R}{E} T^2 e^{-E/RT} \frac{x^2 + 5.347x + 1.376}{x^2 + 7.347x + 10.069} \tag{67}$$

In all these approximations $x = E/RT$.

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