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SOME PROBLEMS CONCERNING THE TEMPERATURE INTEGRAL IN NON-ISOTHERMAL KINETICS

Part II. A new criterion to compare the accuracy of various approximations. A new third order rational approximation

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ABSTRACT

Following their earlier ideas concerning the temperature integral, in order to obtain correct approximations for the temperature integral the authors present a general criterion for the comparison of various approximations as well as a new third order approximation.

INTRODUCTION

In a previous paper [1] the temperature integral

$$I(T, r) = \int_0^T y^r \, e^{-E/Ry} \, dy \tag{1}$$

was approximated through the relationship

$$\int_0^T y^r \, e^{-E/Ry} \, dy = \left(\frac{E}{R}\right)^{r+1} \frac{e^{-x}}{x^{r+2}} Q_r(x) \tag{2}$$

where

$$x = \frac{E}{RT} \tag{3}$$

The function $Q_r(x)$ is an approximate solution of the differential equation

$$Q_r'(x) - \left(1 + \frac{r+2}{x}\right) Q_r(x) + 1 = 0 \tag{4}$$

where $Q_r'(x)$ indicates $dQ_r(x)/dx$. As differential equation (4) does not admit exact solutions a method to obtain approximate solutions was presented in Ref. 1.

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A NEW CRITERION TO COMPARE THE ACCURACY OF VARIOUS APPROXIMATIONS

Let us consider an approximate solution of eqn. (4), $Q_r(x, p)$, where p is a set of constant or variable parameters [1]. Introducing $Q_r(x, p)$ into eqn. (4) we obtain

$$Q_r'(x, p) - \left(1 + \frac{r+2}{x}\right)Q_r(x, p) + 1 \equiv \rho_r(x, p) \tag{5}$$

where the function $\rho_r(x, p)$ appears due to the approximate character of $Q_r(x, p)$.

In order to obtain a relationship between $\rho_r(x, p)$ and the error $\epsilon(x)$ in the temperature integral corresponding to the use of the approximate function $Q_r(x, p)$ in relationship (2), we shall express $\epsilon(x)$ as follows

$$\epsilon(x) = \left(\frac{E}{R}\right)^{r+1} \frac{e^{-x}}{x^{r+2}} Q_r(x, p) - \int_0^T y^r e^{-E/Ry} \, dy \tag{6}$$

From eqn. (6), taking the derivative with respect to x, one obtains

$$\frac{d\epsilon(x)}{dx} = \left(\frac{E}{R}\right)^{r+1} \frac{e^{-x}}{x^{r+2}} \left[Q_r'(x, p) - \left(1 + \frac{r+2}{x}\right)Q_r(x, p) + 1\right] \tag{7}$$

or, taking into account eqn. (5)

$$\frac{d\epsilon(x)}{dx} = \left(\frac{E}{R}\right)^{r+1} \frac{e^{-x}}{x^{r+2}} \rho_r(x, p) \tag{8}$$

From eqn. (8), through integration between x and ∞ and taking into account that

$$\epsilon(\infty) = 0 \tag{9}$$

we get

$$\int_x^{\infty} d\epsilon(z) = \left(\frac{E}{R}\right)^{r+1} \int_x^{\infty} \frac{e^{-z}}{z^{r+2}} \rho_r(z, p) \, dz \tag{10}$$

which, after performing the detailed calculations, becomes

$$\epsilon(x) = -\left(\frac{E}{R}\right)^{r+1} \int_x^{\infty} \frac{e^{-z}}{z^{r+2}} \rho_r(z, p) \, dz \tag{11}$$

which is the desired relationship between $\epsilon(x)$ and $\rho_r(x, p)$.

We shall use a theorem concerning the sign of the integral according to which, if the integral retains the sign in the interval of integration, the integral is a number of the same sign as the function [2]. Taking into account this theorem and the obvious inequality

$$\frac{e^{-x}}{x^{r+2}} > 0 \text{ for } x > 0 \tag{12}$$

it is easy to observe that

$$\epsilon(x) < 0 \text{ if } \rho_r(x, p) > 0 \tag{13}$$

and

$$\epsilon(x) > 0 \text{ if } \rho_r(x, p) < 0 \tag{14}$$

The idea valid for most of the approximations that $\rho_r(x, p)$ does not change its sign was accepted. The cases corresponding to the change of sign will be discussed in a future paper.

For a given value of x, the lower the value of $|\rho_r(x, p)|$, the lower is the value of $|\epsilon(x)|$; thus in order to compare the approximations it is enough to compare the values of the corresponding $\rho_r(x, p)$ without having to evaluate numerically the integral in eqn. (11).

Table 1 lists some approximations, for $r = 0$, taken from [1] and the corresponding functions $\rho(x, p)$ for various values of x.

The comparison between the data given in Table 1 and those listed in Table 3 of Ref. 1 shows that the sign inequalities (13) and (14) are fulfilled and that the values $\rho(x, p)$ can be used in order to compare various approximations of the temperature integral.

The relative error of the temperature integral

$$\epsilon_{\%}(x) = \frac{\epsilon(x)}{\int_0^T y^r \, e^{-E/Ry} \, dy} \times 100 \tag{15}$$

taking into account that

$$\int_0^T y^r \, e^{-E/Ry} \, dy = \left(\frac{E}{R}\right)^{r+1} \frac{e^{-x}}{x^{r+2}} Q_r(x, p) \tag{16}$$

and relationship (11), turns into

$$\epsilon_{\%}(x) = -\frac{\int_x^{\infty} \frac{e^{-z}}{z^{r+2}} \rho_r(z, p) \, dz}{\frac{e^{-x}}{x^{r+2}} Q_r(x, p)} \times 100 \tag{17}$$

The approximate evaluation of the integral from eqn. (17) still remains an open problem.

ON A NEW THIRD ORDER RATIONAL APPROXIMATION

The second order rational approximation valid in principle for any r

$$Q_r(x) \approx \frac{x^2 + x(4 + r)}{x^2 + x(6 + 2r) + (r + 3)(r + 2)} \tag{18}$$

was suggested in our earlier paper [1].

TABLE 1

Values of (x, p) for several of the usual approximations taken from [1]

Approximation	$Q_0(x, p)$	$\rho_0(x, p)$	$x=5$	$x=10$	$x=20$	$x=30$	$x=40$	$x=50$	$x=75$	$x=100$
1	1	$-\frac{2}{x}$	-4.0×10^{-1}	-2.0×10^{-1}	-1.0×10^{-1}	-6.7×10^{-2}	-5.0×10^{-2}	-4.0×10^{-2}	-2.7×10^{-2}	-2.0×10^{-2}
2	$\frac{x-2}{x}$	$\frac{6}{x^2}$	2.4×10^{-1}	6.0×10^{-2}	1.5×10^{-2}	6.7×10^{-3}	3.8×10^{-3}	2.4×10^{-3}	1.1×10^{-3}	6.0×10^{-4}
3	$\frac{x}{x+2}$	$\frac{2}{(x+2)^2}$	4.1×10^{-2}	1.4×10^{-2}	4.1×10^{-3}	2.0×10^{-3}	1.1×10^{-3}	7.4×10^{-4}	3.4×10^{-4}	1.9×10^{-4}
4	$\frac{x+1}{x+3}$	$\frac{-6}{x(x+3)^2}$	-1.9×10^{-2}	-3.6×10^{-3}	-5.7×10^{-4}	-1.8×10^{-4}	-8.1×10^{-5}	-4.3×10^{-5}	-1.3×10^{-5}	-5.7×10^{-6}
5	$\frac{x^2+4x}{x^2+6x+6}$	$\frac{12}{(x^2+6x+6)^2}$	3.2×10^{-3}	4.4×10^{-4}	4.3×10^{-5}	1.0×10^{-5}	3.5×10^{-6}	1.5×10^{-6}	3.2×10^{-7}	1.1×10^{-7}

In order to derive a third order rational approximation we shall start from an approximation of the following form

$$Q_r(x,\ p) \equiv Q_r[x,\ b(x),\ c_i] = \frac{x^2 + ax + b(x)}{x^2 + cx + d} \tag{19}$$

obtained from eqn. (18) through generalisation.

Using the procedure suggested in Ref. 1 we have

$$i = 3 \tag{20}$$

$$c_1 = a;\ c_2 = c;\ c_3 = d \tag{21}$$

The term $b_0(x,\ a,\ c,\ d)$ will be sought by solving the equation [1]

$$\frac{\partial Q_r[x,\ b_0(x,\ a,\ c,\ d),\ a,\ c,\ d]}{\partial x} = \left(1 + \frac{r+2}{x}\right) Q_r[x,\ b_0(x,\ a,\ c,\ d),\ a,\ c,\ d] + 1 = 0 \tag{22}$$

Substituting eqn. (19) in eqn. (22) we get

$$\frac{(2x+a)(x^2+cx+d) - (2x+c)[x^2+ax+b_0(x,\ a,\ c,\ d)]}{(x^2+cx+d)^2} - \left(1 + \frac{r+2}{x}\right)\frac{[x^2+ax+b_0(x,\ a,\ c,\ d)]}{x^2+cx+d} + 1 = 0 \tag{23}$$

an equation whose solution with respect to $b_0(x,\ a,\ c,\ d)$ is

$$b_0(x,\ a,\ c,\ d) = \frac{(x^2+cx+d)[x^3+x^2(c+2)+x(a+d)]}{x^3+x^2(c+4+r)+x[c(r+3)+d]+(r+2)d} - x^2 - ax \tag{24}$$

Introducing this result into eqn. (19) we obtain the desired approximation

$$Q_r(x,\ p) = \frac{x^3+x^2(c+2)+x(a+d)}{x^3+x^2(c+4+r)+x[c(r+3)+d]+(r+2)d} \tag{25}$$

Taking into account the fact that relationship (19) was obtained from relationship (18) through generalisation, we shall introduce into eqn. (25) the following values for a, c and d

$$a = 4 + r \tag{26}$$

$$c = 6 + 2r \tag{27}$$

$$d = (r+3)(r+2) \tag{28}$$

In such a way we obtain the following final form of the third order approximation

$$Q_r(x)\frac{x^3+x^2(8+2r)+x(r^2+6r+10)}{x^3+x^2(10+3r)+x(r+3)(8+3r)+(r+2)^2(r+3)} \tag{29}$$

TABLE 2

The relative errors of the approximations $Q_r(x)$ given by formula (29)

No.	r	$Q_r(x)$	$x=5$	$x=10$	$x=20$	$x=30$	$x=40$	$x=50$	$x=75$	$x=100$
1	0	$Q(x) \cong \frac{x^3+8x^2+10x}{x^3+10x^2+24x+12}$	2.7×10^{-2}	3.3×10^{-3}	2.4×10^{-4}	6.8×10^{-5}	$\approx 10^{-5}$	$\approx 10^{-5}$	$\approx 10^{-5}$	$\approx 10^{-5}$
2	1/2	$Q_{1/2} \cong \frac{x^3+9x^2+13.25x}{x^3+11.5x^2+33.25x+21.875}$	2.7×10^{-2}	3.9×10^{-3}	3.0×10^{-4}	7.5×10^{-5}	$\approx 10^{-5}$	$\approx 10^{-5}$	$\approx 10^{-5}$	$\approx 10^{-5}$
3	1	$Q_1(x) \cong \frac{x^3+10x^2+17x}{x^3+13x^2+44x+36}$	2.6×10^{-2}	4.2×10^{-4}	3.6×10^{-4}	9.1×10^{-5}	$\approx 10^{-5}$	$\approx 10^{-5}$	$\approx 10^{-5}$	$\approx 10^{-5}$
4	3/2	$Q_{3/2} \cong \frac{x^3+11x^2+21.25x}{x^3+14.5x^2+56.25x+55.125}$	2.5×10^{-2}	4.5×10^{-3}	4.5×10^{-4}	1.1×10^{-4}	$\approx 10^{-5}$	$\approx 10^{-5}$	$\approx 10^{-5}$	$\approx 10^{-5}$
5	2	$Q_2(x) \cong \frac{x^3+12x^2+26x}{x^3+16x^2+70x+80}$	2.2×10^{-2}	4.7×10^{-3}	5.0×10^{-4}	1.2×10^{-4}	$\approx 10^{-5}$	$\approx 10^{-5}$	$\approx 10^{-5}$	$\approx 10^{-5}$

Table 2 lists the relative errors corresponding to the approximation (29) for various values of x and r. The reference values of $Q_r(x)$, with which the values of $Q_r(x)$ given by eqn. (29) are compared, have been taken from [1]. The expression "$\simeq 10^{-5}$" means that an accuracy within $2 \times 10^{-5}\%$ is considered as significant [1]. From an inspection of Table 2 one can conclude that the third order approximation given by eqn. (29) leads to very good results. For $r = 1/2$, 1, $3/2$ and 2, the above mentioned approximation is better than all the approximations given in [1]. For $r = 0$ the same approximation is comparable, from the accuracy standpoint, with approximation (10) (Table 3) and eqn. (3) (Table 4), the best of those given in [1].

CONCLUSIONS

1. The relationship (11) between the error of the temperature integral and the function $\rho_r(x, p)$ was derived.
2. It was shown that to compare the accuracy of various approximations it is enough to compare the values of $\rho_r(x, p)$.
3. A new third order rational approximation of the temperature integral was proposed.

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