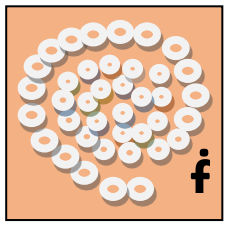

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Chemical kinetics and environmental fate: a quantitative and efficient method for solving the Akzo Nobel problem

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Abstract

This paper presents an in-depth quantitative approach for solving two versions of the chemical Akzo nobel problem. We developed a two–step, fifth–order, self–starting block method for its solution using different literature based initial conditions. We made comparisons with other relevant works in the literature albeit with due diligence ensuring the same equations and initial conditions. Our method outperformed some recent works making it suitable for the numerical solution of other stiff nonlinear ODEs.

Keywords and phrases: Chemical Akzo Nobel; cputime; hybrid method; order of convergence.

1 Introduction

The Chemical Akzo Nobel Problem represents a significant environmental challenge associated with the multinational corporation Akzo Nobel, a leader in paints, coatings, and specialty chemicals. Over the years, concerns have arisen regarding contamination linked to its chemical production facilities, particularly the persistence and transformation of hazardous pollutants [1, 2]. Addressing these issues requires an in-depth understanding of chemical kinetics, which governs the reaction rates, degradation pathways, and transport of contaminants in various environmental matrices [3, 4]. Advanced kinetic modeling can provide crucial insights into the fate of pollutants and optimize remediation strategies [5, 6, 7].

One of the most notable contamination cases occurred at the Akzo Nobel Polymer Chemicals facility in Burt, New York, where the production of organic peroxides led to extensive soil and groundwater pollution [8]. The U. S. Environmental Protection Agency (EPA) identified hazardous volatile organic compounds (VOCs), such as acetone, benzene, chlorobenzene, and methylene chloride, persisting in the environment [9, 10, 11, 12, 13]. Despite natural attenuation and containment measures, the long term presence of these contaminants highlights the role of reaction kinetics, including degradation rates, reaction mechanisms, and the influence of environmental factors such as pH, temperature, and microbial activity [14, 15, 16].

Similarly, at the Akzo Nobel Chemicals facility in Delaware City, Delaware, extensive groundwater contamination prompted regulatory intervention [17, 18]. The EPA proposed remediation measures, including the establishment of a Technical Impracticability Zone and long-term monitoring [12, 19, 20]. However, traditional containment strategies often overlook kinetic parameters such as reaction half-lives, catalytic degradation efficiencies, and the competitive interactions between pollutants and remediation agents [21, 22]. Without a clear understanding of these kinetic aspects, contamination may

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persist beyond predicted timelines, necessitating more robust numerical and experimental approaches [23, 24].

Beyond the U.S., environmental concerns extend internationally. International Paint Limited, an Akzo Nobel subsidiary, was fined £ 650, 000 for the release of tributyltin (TBT) into the River Yealm estuary, UK [25]. The persistence of TBT in aquatic ecosystems underscores the importance of reaction kinetics in heterogeneous systems, where adsorption-desorption equilibria, photodegradation rates, and hydrolysis reactions dictate the longevity of pollutants in water bodies [26].

To mitigate such environmental challenges, Akzo Nobel introduced initiatives like the Priority Substance Program to phase out hazardous chemicals [27]. However, reports indicate that some toxic substances remain in its product portfolio, reinforcing the need for kinetic-based predictive models to evaluate chemical fate and transformation [28]. Additionally, the company's Product Stewardship Strategy aims to manage the life cycle of its chemicals, yet effective implementation depends on a precise understanding of reaction rate constants, activation energies, and catalytic degradation mechanisms [29].

Despite these initiatives, the Chemical Akzo Nobel Problem persists as a complex issue requiring innovative kinetic modeling and computational approaches for effective resolution [30]. Existing regulatory frameworks often lack reaction-rate- based assessments, leading to underestimated contamination persistence and ineffective remediation efforts]. This study proposes a fifth-order block hybrid method integrating chemical kinetics with numerical simulations to enhance predictive accuracy in contamination dispersion and degradation [31].

The Akzo Nobel problem consists of six stiff nonlinear differential equations. However, their stiffness and nonlinearity makes them difficult to solve accurately and efficiently. This paper aims to develop an efficient method for solving these stiff differential equations, ensuring accurate and reliable results.

2 Methodology

A $k-$step first derivative block hybrid method for the solution of ordinary differential equations is [33],

$$y(x) = \sum_{j=0}^{k} \alpha_j y_{n+j} + h \sum_{j=0}^{k} \beta_j f_{n+j}, \tag{1}$$

and

$$y(x) = \sum_{j=0}^{k} \alpha_j y_{n+j} + h \sum_{j=0}^{k} \beta_j f_{n+j}, \tag{2}$$

where the α_j, β_j are unknown polynomials, $y_{n+j} = y(x_n + jh)$, is an approximate solution

$$y^{'}(x_{n+j}) = f_{n+j} = f(x_n + jh, y(x_n + jh)).$$

Besides, the continuous coefficients are

$$\alpha_j(x) = \sum_{j=0}^{k} \alpha_{j,j+1} x^j, \qquad \beta_j(x) = \sum_{j=0}^{k} \beta_{j,j+1} x^j, \quad \text{for} \quad j = 0, 1, \cdots, k-1.$$

The following matrix equation $DC = I$, is solved where $I \in \mathbb{R}^{(t+m)\times(t+m)}$ is an identity matrix, D and C are real $(t+m) \times (t+m)$ matrices (t interpolation points $0 < t \leq k$) and m collocation points, to obtain $\alpha_j(x)$ and $\beta_j(x)$ which are the first rows of C [32].

2.1 First derivative block hybrid method

Let $y_n = y(x_n)$ and $f_n = f(x_n, y_n)$, $y_{n+i} = y(x_{n+i}) = y(x_n + ih)$, for $x_i = x_0 + ih, i \in \{1, \frac{4}{3}, \frac{5}{3}, 2\}$, $h = \frac{b-a}{4}$, $f_{n+i} = f(x_{n+i}, y_{n+i}) = f(x_n + ih, y(x_n + ih))$. By making the substitution $t = 1, m = 5$

and the above into (1), we obtained the continuous formulation:

$$y(x) = \alpha_0(x)y_n + h\left[\beta_0(x)f_n + \beta_1(x)f_{n+1} + \beta_{\frac{4}{3}}(x)f_{n+\frac{4}{3}} + \beta_{\frac{5}{3}}(x)f_{n+\frac{5}{3}} + \beta_2(x)f_{n+2}\right]. \quad (3)$$

The matrix D in [32] becomes:

$$D = \begin{bmatrix} 1 & x_n & x_n^2 & x_n^3 & x_n^4 & x_n^5 \\ 0 & 1 & 2x_n & 3x_n^2 & 4x_n^3 & 5x_n^4 \\ 0 & 1 & 2x_{n+1} & 3x_{n+1}^2 & 4x_{n+1}^3 & 5x_{n+1}^4 \\ 0 & 1 & 2x_{n+\frac{4}{3}} & 3x_{n+\frac{4}{3}}^2 & 4x_{n+\frac{4}{3}}^3 & 5x_{n+\frac{4}{3}}^4 \\ 0 & 1 & 2x_{n+\frac{5}{3}} & 3x_{n+\frac{5}{3}}^2 & 4x_{n+\frac{5}{3}}^3 & 5x_{n+\frac{5}{3}}^4 \\ 0 & 1 & 2x_{n+2} & 3x_{n+2}^2 & 4x_{n+2}^3 & 5x_{n+2}^4 \end{bmatrix}. \quad (4)$$

We replaced x_n with $x_{n+1} - h$, $x_{n+\frac{4}{3}} = x_{n+1} + \frac{h}{3}$, $x_{n+\frac{5}{3}} = x_{n+1} + \frac{2h}{3}$, $x_{n+2} = x_{n+1} + h$, so the determinant of D becomes $\det(D) = \frac{6400}{729}h^{10}$.

Lemma 2.1. *Let ϵ be a small but positive real number i.e., $\epsilon > 0$, then $h > \left[\frac{729\epsilon}{6400}\right]^{\frac{1}{10}}$. Besides, if ϵ is chosen to be 2^{-52}, the step size h is greater than 0.021893, then D has nonzero pivots.*

Proof. Since by assumption $\epsilon > 0$ then let

$$\frac{6400h^{10}}{729} > \epsilon.$$

This implies that

$$h^{10} > \left[\frac{729\epsilon}{6400}\right],$$

and

$$h > \left[\frac{729\epsilon}{6400}\right]^{\frac{1}{10}}.$$

Now, substituting $\epsilon = 2^{-52}$ yields

$$h > \left[\frac{729}{6400}\right]^{\frac{1}{10}} = \left[\frac{729 \times 2^{-52}}{6400}\right]^{\frac{1}{10}} = 0.021893.$$

Therefore, if $h > 0.021893$ then the determinant of D will be nonzero, ensuring the non−singularity of D.

Now, we can find the inverse matrix C from (4) where I is the six by six identity matrix. The elements on the first row of the C matrix makes up the continuous coefficients used to evaluate the continuous

formulation with $w = x_{n+1} - x$:

$$\begin{aligned} y(x) = y_n &+ \left(\frac{-54w^5 - 135hw^4 - 110h^2w^3 - 30h^3w^2 + 329h^5}{1200h^4}\right) f_n \\ &+ \left(\frac{108w^5 + 135hw^4 - 140h^2w^3 - 270h^3w^2 - 120h^4w + 287h^5}{120h^4}\right) f_{n+1} \\ &+ \left(\frac{-162w^5 - 135hw^4 + 270h^2w^3 + 270h^3w^2 - 243h^5}{80h^4}\right) f_{n+\frac{4}{3}} \\ &+ \left(\frac{324w^5 + 135hw^4 - 540h^2w^3 - 270h^3w^2 + 351h^5}{200h^4}\right) f_{n+\frac{5}{3}} \\ &+ \left(\frac{-27w^5 + 35h^2w^3 + 15h^3w^2 - 23h^5}{60h^4}\right) f_{n+2}. \end{aligned}$$

We evaluate the continuous scheme at $w = 0, -\frac{h}{3}, -\frac{2}{3}$ and $-h$. In essence, for $w = 0$, using $w = x_{n+1} - x$, $x = x_{n+1} + 0 = x_{n+1}$ which is same as $y(x) = y(x_{n+1}) = y_{n+1}$, and for $w = -\frac{h}{3}$, with $w = x_{n+1} - x, x = x_{n+1} + \frac{h}{3} = x_{n+\frac{4}{3}}$. Hence, $y(x) = y(x_{n+\frac{4}{3}}) = y_{n+\frac{4}{3}}$. If $w = -\frac{2h}{3}$, $\text{-}\frac{2h}{3} = x_{n+1} - x$, and $x = x_{n+1} + \frac{2h}{3} = x_{n+\frac{5}{3}}$ and for $w = -h$, with $w = x_{n+1} - x$, $x = x_{n+1} + h = x_{n+2}$. Finally,

$$y(x) = y(x_{n+2}) = y_{n+2}.$$

Evaluating the continuous scheme in equation (3), we obtained the schemes

$$y_{n+1} = y_n + \frac{329h}{1200} f_n + \frac{287h}{120} f_{n+1} - \frac{243h}{80} f_{n+\frac{4}{3}} + \frac{351h}{200} f_{n+\frac{5}{3}} - \frac{23h}{60} f_{n+2}, \tag{5}$$

$$y_{n+\frac{4}{3}} = y_n + \frac{554hf_n}{2025} f_n + \frac{1024h}{405} f_{n+1} - \frac{14h}{5} f_{n+\frac{4}{3}} + \frac{128h}{75} f_{n+\frac{5}{3}} - \frac{152h}{405} f_{n+2}, \tag{6}$$

$$y_{n+\frac{5}{3}} = y_n + \frac{355h}{1296} f_n + \frac{1625h}{648} f_{n+1} - \frac{125h}{48} f_{n+\frac{4}{3}} + \frac{15h}{8} f_{n+\frac{5}{3}} - \frac{125h}{324} f_{n+2}, \tag{7}$$

$$y_{n+2} = y_n + \frac{41h}{150} f_n + \frac{38h}{15} f_{n+1} - \frac{27h}{10} f_{n+\frac{4}{3}} + \frac{54h}{25} f_{n+\frac{5}{3}} - \frac{4h}{15} f_{n+2}. \tag{8}$$

2.2 Order and Consistency of the Method.

In this section, we examined the order, error constant, zero-stability, consistency and convergence of the block yybrid method under discussion:

$$\alpha_0 = -\begin{bmatrix} 1 \\ 1 \\ 1 \\ 1 \end{bmatrix}, \alpha_1 = \begin{bmatrix} 1 \\ 0 \\ 0 \\ 0 \end{bmatrix}, \alpha_{\frac{4}{3}} = \begin{bmatrix} 0 \\ 1 \\ 0 \\ 0 \end{bmatrix}, \alpha_{\frac{5}{3}} = \begin{bmatrix} 0 \\ 0 \\ 1 \\ 0 \end{bmatrix}, \alpha_2 = \begin{bmatrix} 0 \\ 0 \\ 0 \\ 1 \end{bmatrix},$$

In the same vein,

$$\beta_0 = \begin{bmatrix} \frac{329}{1200} \\ \frac{554}{2025} \\ \frac{355}{1296} \\ \frac{41}{150} \end{bmatrix}, \beta_1 = \begin{bmatrix} \frac{287}{120} \\ \frac{1024}{405} \\ \frac{1625}{648} \\ \frac{38}{15} \end{bmatrix}, \beta_{\frac{4}{3}} = \begin{bmatrix} -\frac{243}{80} \\ -\frac{14}{5} \\ -\frac{125}{48} \\ -\frac{27}{10} \end{bmatrix}, \beta_{\frac{5}{3}} = \begin{bmatrix} \frac{351}{200} \\ \frac{128}{75} \\ \frac{15}{8} \\ \frac{54}{25} \end{bmatrix}, \beta_2 = \begin{bmatrix} -\frac{23}{60} \\ -\frac{152}{405} \\ -\frac{125}{324} \\ -\frac{4}{15} \end{bmatrix}.$$

In order to obtain the error constant and order of the new schemes, we substituted the vectors in:

$$
\begin{aligned}
C_0 &= \alpha_0 + \alpha_1 + \alpha_{\frac{4}{3}} + \alpha_{\frac{5}{3}} + \alpha_2 = 0,\\
C_1 &= \left[\alpha_1 + \left(\frac{4}{3}\right)^1 \alpha_{\frac{4}{3}} + \left(\frac{5}{3}\right)^1 \alpha_{\frac{5}{3}} + 2^1\alpha_2\right]\\
&\quad - \left[\beta_0 + \beta_1 + \beta_{\frac{4}{3}} + \beta_{\frac{5}{3}} + \beta_2\right] = 0,\\
C_2 &= \frac{1}{2!}\left[\alpha_1 + \left(\frac{4}{3}\right)^2 \alpha_{\frac{4}{3}} + \left(\frac{4}{3}\right)^2 \alpha_{\frac{5}{3}} + 2^2\alpha_2\right]\\
&\quad - \left[\beta_1 + \left(\frac{4}{3}\right)\beta_{\frac{4}{3}} + \left(\frac{5}{3}\right)\beta_{\frac{5}{3}} + 2\beta_2\right] = 0,\\
C_3 &= \frac{1}{3!}\left[\alpha_1 + \left(\frac{4}{3}\right)^3 \alpha_{\frac{4}{3}} + \left(\frac{5}{3}\right)^3 \alpha_{\frac{5}{3}} + 2^3\alpha_2\right]\\
&\quad - \frac{1}{2!}\left[\beta_1 + \left(\frac{4}{3}\right)^2 \beta_{\frac{4}{3}} + \left(\frac{5}{3}\right)^2 \beta_{\frac{5}{3}} + 2^2\beta_2\right] = 0\\
,C_4 &= \frac{1}{4!}\left[\alpha_1 + \left(\frac{4}{3}\right)^4 \alpha_{\frac{4}{3}} + \left(\frac{5}{3}\right)^4 \alpha_{\frac{5}{3}} + 2^4\alpha_2\right]\\
&\quad - \frac{1}{3!}\left[\beta_1 + \left(\frac{4}{3}\right)^3 \beta_{\frac{4}{3}} + \left(\frac{5}{3}\right)^3 \beta_{\frac{5}{3}} + 2^3\beta_2\right] = 0,\\
C_5 &= \frac{1}{5!}\left[\alpha_1 + \left(\frac{4}{3}\right)^5 \alpha_{\frac{4}{3}} + \left(\frac{5}{3}\right)^5 \alpha_{\frac{5}{3}} + 2^5\alpha_2\right]\\
&\quad - \frac{1}{4!}\left[\beta_1 + \left(\frac{4}{3}\right)^4 \beta_{\frac{4}{3}} + \left(\frac{5}{3}\right)^4 \beta_{\frac{5}{3}} + 2^4\beta_2\right] = 0,\\
C_6 &= \frac{1}{6!}\left[\alpha_1 + \left(\frac{4}{3}\right)^6 \alpha_{\frac{4}{3}} + \left(\frac{5}{3}\right)^6 \alpha_{\frac{5}{3}} + 2^6\alpha_2\right]\\
&\quad - \frac{1}{5!}\left[\beta_1 + \left(\frac{4}{3}\right)^5 \beta_{\frac{4}{3}} + \left(\frac{5}{3}\right)^5 \beta_{\frac{5}{3}} + 2^5\beta_2\right] \neq 0.
\end{aligned}
$$

Thus,

$$C_0 = C_1 = C_2 = C_3 = C_4 = C_5 = 0 \text{ and } C_6 \neq 0.$$

Hence, since C_6 is non-zero, this indicates that the error constant of the System is:

$$\text{Error Constant} = C_6 = \begin{bmatrix} \frac{49}{12600} \\ \frac{368}{164025} \\ \frac{475}{209952} \\ \frac{1}{450} \end{bmatrix} \tag{9}$$

The order and error constants for the constructed block hybrid methods are presented in Table 1. It is clear from the table that the members of the block hybrid method without a second-derivative evaluation are all of order five.

2.3 Order Of Convergence

We examine the order of convergence of the newly derived block hybrid method. We begin by showing this well known definition of Lipschitz condition which will be used shortly.

Table 1: The table below shows the error constants of the new discrete schemes.

y_i	Order	Error Constant $C_6 \neq 0$
y_{n+1}	5	$2.268518518518519 \times 10^{-3}$
$y_{n+\frac{4}{3}}$	5	$2.243560432860844 \times 10^{-3}$
$y_{n+\frac{5}{3}}$	5	$2.262421886907484 \times 10^{-3}$
y_{n+2}	5	$2.222222222222222 \times 10^{-3}$

Definition 2.2. *A function $f(x,y)$ satisfies the lipschitz condition on a domain $D \subseteq \Re^2$, if there exists a constant $L > 0$ such that:*

$$\mid f(x,y) - f(x,y^*) \mid \leq L \mid y - y^* \mid,$$

for all $(x,y),(x,y^*) \in D$.

In the same vein, we define the convergence as used above.

Definition 2.3. *A LMM is said to be convergent if, for all initial value problems subject to the above Lipschitz condition:*

$$\lim_{h \to 0} y_n = y^*(x_n),$$

for all solutions $\{y_n\}$ of the method.

Assuming the exact solution of y_{n+1} is:

$$y^*_{n+1} = y^*_n + \frac{329hf_n}{1200} + \frac{287hf_{n+1}}{120} - \frac{243hf_{n+\frac{4}{3}}}{80} + \frac{351hf_{n+\frac{5}{3}}}{200} - \frac{23hf_{n+2}}{60} + \frac{49}{12600}h^6 y^{*(6)}(\xi_n) + R_7,$$

where R_6 is the remainder term. Let the exact solution of y_{n+2} be

$$y^*_{n+2} = y_n + \frac{41hf_n}{150} + \frac{38hf_{n+1}}{15} - \frac{27hf_{n+\frac{4}{3}}}{10} + \frac{54hf_{n+\frac{5}{3}}}{25} - \frac{4hf_{n+2}}{15} + \frac{1}{450}h^6 y^{*(6)}(\xi_n) + R_7,$$

and so on and so forth. After subtracting y_{n+1} from y^*_{n+1}, we obtained

$$\begin{aligned} y^*_{n+1} - y_{n+1} = y^*_n &+ \left[\frac{329hf_n}{1200} + \frac{287hf_{n+1}}{120} - \frac{243hf_{n+\frac{4}{3}}}{80} + \frac{351hf_{n+\frac{5}{3}}}{200} - \frac{23hf_{n+2}}{60}\right] \\ &- y_n - \left[\frac{329hf_n}{1200} + \frac{287hf_{n+1}}{120} - \frac{243hf_{n+\frac{4}{3}}}{80} + \frac{351hf_{n+\frac{5}{3}}}{200} - \frac{23hf_{n+2}}{60}\right] \\ &+ \frac{49}{12600}h^6 y^{*(6)}(\xi_n) + R_7. \end{aligned}$$

Expanding the above,

$$\begin{aligned} y^*_{n+1} - y_{n+1} = y^*_n - y_n \\ &+ \frac{329}{1200}[f(x_n, y^*_n) - f(x_n, y_n)] \\ &+ \frac{287h}{120}\left[f(x_{n+1}, y^*_{n+1}) - f(xn+1, y_{n+1})\right] \\ &- \frac{243h}{80}\left[f(x_{n+\frac{4}{3}}, y^*_{n+\frac{4}{3}}) - f(x_{n+\frac{4}{3}}, y_{n+\frac{4}{3}})\right] \\ &+ \frac{351h}{200}[f(x_{n+\frac{5}{3}}, y^*_{n+\frac{5}{3}}) - f(x_{n+\frac{5}{3}}, y_{n+\frac{5}{3}})] \\ &- \frac{23h}{60}\left[f(x_{n+2}, y^*_{n+2}) - f(xn+2, y_{n+2})\right] \\ &+ \frac{49}{12600}h^6 y^{*(6)}(\xi_n) + R_7. \end{aligned}$$

Let $d_n = y^*_n - y_n, d_{n+\frac{4}{3}} = y^*_{n+\frac{4}{3}} - y_{n+\frac{4}{3}}, d_{n+1} = y^*_{n+1} - y_{n+1}$ etc. Taking the absolute values of both sides, using the triangular inequality and imposing appropriate Lipschitz conditions yields

$$\begin{aligned} d_{n+1} \leq \left(1 + \frac{329}{1200}L\right) \mid d_n \mid + \frac{287h}{120}L \mid d_{n+1} \mid + \frac{243h}{80}L \mid d_{n+\frac{4}{3}} \mid + \frac{351h}{200}L \mid d_{n+\frac{5}{3}} \mid \\ + \frac{23h}{60}L|d_{n+2}| + \frac{49h^6}{12600}|y^*_n - y_n|. \end{aligned}$$

This simplifies to:

$$\begin{aligned} \left(1 - \frac{287h}{120}L\right) \mid d_{n+1} \mid \leq \left(1 - \frac{329h}{1200}L\right) \mid d_n \mid + \frac{243h}{80}L \mid d_{n+\frac{4}{3}} \mid + \frac{351h}{200}L \mid d_{n+\frac{5}{3}} \mid + \frac{23h}{60}L \mid d_{n+2} \mid \\ + \frac{49h^6}{12600} \mid y^{*6}_n(\xi_n) \mid + O(h^7). \end{aligned}$$

As $h \to 0$, with the exception of $\mid d_n \mid$ every other term on the right hand side tends to zero while on the left hand side, we are left with $\mid d_{n+1} \mid$ and by the definition of convergence,

$$\lim_{h \to 0} y_{n+1} = y^*_{n+1}.$$

Subtract y_{n+2} from y^*_{n+2} to obtain

$$\begin{aligned} y^*_{n+2} - y_{n+2} = y^*_n + \left[\frac{41hf_n}{150} + \frac{38hf_{n+1}}{15} - \frac{27hf_{n+\frac{4}{3}}}{10} + \frac{54hf_{n+\frac{5}{3}}}{25} - \frac{4hf_{n+2}}{15}\right] \\ - y_n - \left[\frac{41hf_n}{150} + \frac{38hf_{n+1}}{15} - \frac{27hf_{n+\frac{4}{3}}}{10} + \frac{54hf_{n+\frac{5}{3}}}{25} - \frac{4hf_{n+2}}{15}\right] \\ + \frac{1}{450}h^6 y^{*(6)}(\xi_n) + R_7. \end{aligned}$$

Expanding the above,

$$\begin{aligned} y^*_{n+2} - y_{n+2} = y^*_n - y_n \\ &+ \frac{41}{150}[f(x_n, y^*_n) - f(x_n, y_n)] \\ &+ \frac{38h}{15}\left[f(x_{n+1}, y^*_{n+1}) - f(x_{n+1}, y_{n+1})\right] \\ &- \frac{27h}{10}\left[f(x_{n+\frac{4}{3}}, y^*_{n+\frac{4}{3}}) - f(x_{n+\frac{4}{3}}, y_{n+\frac{4}{3}})\right] \\ &+ \frac{54h}{25}[f(x_{n+\frac{5}{3}}, y^*_{n+\frac{5}{3}}) - f(x_{n+\frac{5}{3}}, y_{n+\frac{5}{3}})] \\ &- \frac{4h}{15}\left[f(x_{n+2}, y^*_{n+2}) - f(x_{n+2}, y_{n+2})\right] \\ &+ \frac{h^6}{450}y^{*(6)}(\xi_n) + R_7. \end{aligned}$$

In the same vein,

$$\begin{aligned} d_{n+2} \leq \left(1 + \frac{41}{150}L\right) \mid d_n \mid + \frac{38h}{15}L \mid d_{n+1} \mid + \frac{27h}{10}L \mid d_{n+\frac{4}{3}} \mid + \frac{54h}{25}L \mid d_{n+\frac{5}{3}} \mid \\ + \frac{4h}{15}L \mid d_{n+2} \mid + \frac{h^6}{450} \mid y^*_n - y_n \mid . \end{aligned}$$

The above expression reduces to

$$\begin{aligned} \left(1 - \frac{4h}{15}L\right) \mid d_{n+2} \mid \leq \left(1 - \frac{41h}{150}L\right) \mid d_n \mid + \frac{38h}{15}L \mid d_{n+1} \mid + \frac{27h}{10}L \mid d_{n+\frac{4}{3}} \mid \\ + \frac{54h}{25}L \mid d_{n+\frac{5}{3}} \mid + \frac{h^6}{450} \mid y^{*6}_n(\xi_n) \mid + O(h^7). \end{aligned}$$

As $h \to 0$, $\mid d_{n+2} \mid \leq \mid d_n \mid$ and $y^*_{n+2} - y^*_n = y_{n+2} - y_n$ is satisfied. The convergence of y_{n+2} is established in agreement with [23]. In the same vain, it can be shown that the other y_{n+i}'s for $i \in \left\{\frac{4}{3}, \frac{5}{3}\right\}$ converge. Hence, we have shown that the new block hybrid method is convergent. The remainder term R_6 which is

$$R_{p+1} = C_{p+2}h^{p+2}y^{*(p+2)}(\xi) = \underline{o}(h^7).$$

Hence, the order of convergence of the new method is $p + 2$ which is seven.

2.4 Region of absolute stability.

Generally, in designing a new numerical method, it is very important to consider the stability properties of the methods. We plotted the region of absolute stability of the new method using the stability polynomial. To get the stability polynomial which we used in plotting the region of absolute stability

of the new method in this paper, we reformulate the block hybrid methods in linear multistep form as

$$\begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} y_{n+1} \\ y_{n+\frac{4}{3}} \\ y_{n+\frac{5}{3}} \\ y_{n+2} \end{bmatrix} = \begin{bmatrix} 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} y_{n-1} \\ y_{n-2} \\ y_{n-3} \\ y_n \end{bmatrix}$$
$$+ \begin{bmatrix} \frac{287}{120} & -\frac{243}{80} & \frac{351}{200} & -\frac{23}{60} \\ \frac{1024}{405} & -\frac{14}{5} & \frac{128}{75} & -\frac{152}{405} \\ \frac{1625}{468} & -\frac{125}{48} & \frac{15}{8} & -\frac{125}{324} \\ \frac{38}{15} & -\frac{27}{10} & \frac{54}{25} & -\frac{4}{15} \end{bmatrix} \begin{bmatrix} f_{n+1} \\ f_{n+\frac{4}{3}} \\ f_{n+\frac{5}{3}} \\ f_{n+2} \end{bmatrix}$$
$$+ \begin{bmatrix} 0 & 0 & 0 & \frac{329}{1200} \\ 0 & 0 & 0 & \frac{554}{2025} \\ 0 & 0 & 0 & \frac{355}{1296} \\ 0 & 0 & 0 & \frac{41}{150} \end{bmatrix} \begin{bmatrix} f_{n-1} \\ f_{n-2} \\ f_{n-3} \\ f_n \end{bmatrix}.$$

We also used the following to explain the zero stability of the new method, whereas the matrices are

$$A = \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix}, \quad B = \begin{bmatrix} 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 1 \end{bmatrix},$$

$$F = \begin{bmatrix} \frac{287}{120} & -\frac{243}{80} & \frac{351}{200} & -\frac{23}{60} \\ \frac{1024}{405} & -\frac{14}{5} & \frac{128}{75} & -\frac{152}{405} \\ \frac{1625}{648} & -\frac{125}{48} & \frac{15}{8} & -\frac{125}{324} \\ \frac{38}{15} & -\frac{27}{10} & \frac{54}{25} & -\frac{4}{15} \end{bmatrix}, \quad J = \begin{bmatrix} 0 & 0 & 0 & \frac{329}{1200} \\ 0 & 0 & 0 & \frac{554}{2025} \\ 0 & 0 & 0 & \frac{355}{1296} \\ 0 & 0 & 0 & \frac{41}{150} \end{bmatrix}.$$

The matrices above are used to find the determinant

$$\rho(w, z) = \det[Aw - B - Jz - Fzw],$$

where $y' = \lambda y, z = \lambda h$ is the usual test equation, $w = e^{i\theta} = -1$ and $\theta \in [0, \pi]$. This results in the following stability polynomial

$$\det\left(Aw - B - Jz - Fzw\right) = \frac{((20w^4 - 2w^3)z^4 + (-(114w^4) - 24w^3)z^3 + (357w^4 - 141w^3)z^2}{540}$$
$$+ \frac{(-(648w^4) - 432w^3)z + 540w^4 - 540w^3}{540}.$$

The above polynomial which is the stability polynomial is used to plot the region of absolute stability using octave and the result is shown in Figure 1 which is A–stable.

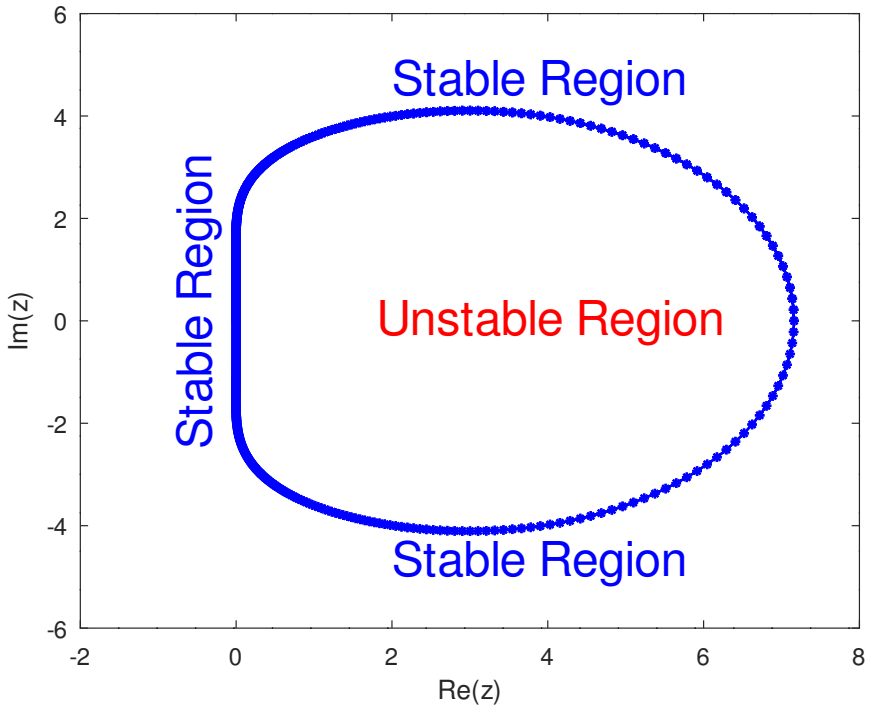

Figure 1: Region of absolute stability of the method.

To describe the zero stability of the method, we find the zeros of

$$\det[rA - B] = r^4 - r^3 = r^3(r-1).$$

Hence, the roots are $r = 0$ (thrice) and $r = 1$ (simple). Therefore, our method is zero stable, consistent and convergent by definition [34].

3 Numerical simulations and discussion

In this section, we compared the performances of the new block hybrid method with the pre-existing hybrid methods. Throughout this section, all the results are self explanatory.

Example 3.1. Kaps Problem This is a well known problem and we are using it to test our method since it has an exact solution. The differential equations are $y_1 = -1002y_1(x) + 1000y_2^2(x)$, and $y_2 = y_1(x) - y_2(x)^2 - y_2(x)$ satisfying $y_1(0) = 1$, and $y_2(0) = 1$. For $h = 0.1$, we compared our solution[8825] with those in the literature.

The results of our method applied on this problem is presented in Tables 2 and 3. In comparison to the works of Yakubu et al. [35], as shown in Table 3, it is a no brainer that our method outperformed their's as depicted in columns three and seven. Furthermore, a closer look at the same table showed that the new method gave a smaller error by a factor of respectively 0.9723, 0.9277, 0.9725, 0.8070 when compared with column four in an earlier work by the first author [36]. Lastly, from Table 3, the error of our method is smaller when compared to those of [38] and [39] in absolute value sense.

Example 3.2. Chemical AKZO Nobel Problem
The Chemical AKZO problem arose from the AKZO Nobel Central Research in Arnhem, Holland [37]. The problem describes a chemical process, in which two species, FBL and ZUL, are mixed, while Carbon (IV) Oxide is continuously added. The resulting species of importance is ZAL. The names

[8825] The exact solution is $y_1(x) = \exp(-2x)$ and $y_2(x) = \exp(-x)$.

Table 2: Absolute error of the Kaps problem when compared with the exact solution.

x	y	Absolute Error
5	y_1	$4.7063607470752025\times10^{-07}$
	y_2	$4.8980745824718508\times10^{-08}$
10	y_1	$2.1367340022195365\times10^{-11}$
	y_2	$3.2449617970962963\times10^{-10}$
20	y_1	$4.4043129134540812\times10^{-20}$
	y_2	$1.4300959134127165\times10^{-14}$
30	y_1	$9.0783278425106747\times10^{-29}$
	y_2	$6.2969962352740103\times10^{-19}$
40	y_1	$1.8712575128713415\times10^{-37}$
	y_2	$2.7700163840899019\times10^{-23}$
50	y_1	$3.8571031302102944\times10^{-46}$
	y_2	$1.2172633338013624\times10^{-27}$

Table 3: Absolute error of the Kaps problem solved using our method when compared with some results in the literature. NA means Not Available.

x	y_i	Yakubu et al. [35]	Akinola et al. [36]	3POBBDF(5) [38]	Error in [39]	New Method
5	y_1	1.22×10^{-03}	4.84×10^{-07}	NA	NA	4.70×10^{-07}
	y_2	1.29×10^{-06}	5.28×10^{-08}	NA	NA	4.89×10^{-08}
50	y_1	3.32×10^{-05}	3.96×10^{-46}	7.38×10^{-24}	7.14×10^{-21}	3.85×10^{-46}
	y_1	9.88×10^{-08}	1.50×10^{-27}	4.83×10^{-25}	3.34×10^{-19}	1.21×10^{-27}

of the reactants are dummy 'variables' due to the commercial competition in this field. The chemical reactions are as listed below,

$$2FBL + \frac{1}{2}CO_2 \xrightarrow{k_1} FBLT + H_2O$$

$$ZAL + FBL \underset{k_2}{\overset{\frac{k_2}{K}}{\rightleftharpoons}} FBLT + ZUH$$

$$\begin{aligned} FBL + 2ZUH + CO_2 &\xrightarrow{k_3} BL + \text{nitrate} \\ FBL.ZUH + \frac{1}{2}CO_2 &\xrightarrow{k_4} ZAL + H_2O \\ FBL + ZUH &\rightleftharpoons FBLT.ZUH, \end{aligned}$$

where $K_s = \dfrac{[FBL.ZUH]}{[FBL].[ZUH]} = 115.83$ is an equilibrium constant and brackets refers to concentrations. The relation between mathematical and chemical formulation is $y_1 = [FBL], y_2 = [CO_2], y_3 = [FBLT], y_4 = [ZUH], y_5 = [ZAL]$ and $y_6 = [FBL.ZUH]$. The velocities of the system of chemical

equations are given by:

$$\begin{aligned} r_1 &= k_1 y_1^4 \sqrt{y_2}, \\ r_2 &= k_2 y_3 y_4, \\ r_3 &= \frac{k_2}{K_s} y_3 y_5, \\ r_4 &= k_3 y_1 y_4^2, \\ r_5 &= k_4 y_6^2 \sqrt{y_2}, \\ F_{in} &= \text{klA}\left(\frac{\rho(O_2)}{H} - y_2\right), \end{aligned}$$

where $k_1 = 18.7, k_2 = 0.58, k_3 = 0.009, k_4 = 0.42, klA = 3.3, H = 737, K = 34.4$ and $\rho(O_2) = 0.9$. The mathematical model is stiff and consists of six non-linear system of ordinary differential equations:

$$y_1' = -2r_1 + r_2 - r_3 - r_4, \tag{10}$$
$$y_2' = -\frac{1}{2}r_1 - r_4 - \frac{1}{2}r_5 + F_{in}, \tag{11}$$
$$y_3' = r_1 - r_2 + r_3, \tag{12}$$
$$y_4' = -r_2 + r_3 - 2r_4, \tag{13}$$
$$y_5' = r_2 - r_3 + r_5, \tag{14}$$
$$y_6' = K_s y_1 y_2 y_6, \tag{15}$$

satisfying the initial conditions

$$[y_1(0), y_2(0), y_3(0), y_4(0), y_5(0), y_6(0)]^T = [0.44, 0.00123, 0, 0.007, 0, 0]^T \texttt{mol/liter}.$$

In this paper, we present two different versions of the chemical AKZO nobel problem; which consists of six nonlinear ordinary differential equations found in the literature. While the first five differential equations in the two versions are the same, the only marked difference is in the last. The first version has $y_6' = K_s y_1 y_2 y_6$, as the last equation while the second has $y_6' = -k_4 y_6^2 \sqrt{y_2} = -r_5$ [40].

In solving the first version of the problem, we used three different initial conditions: $[0.44, 0.00123, 0, 0.007, 0, 0]^T$ as in [37], which proved to be unrealistic, $[0.44, 0.00123, 0, 0, 0, 0.007]^T$ as in [37], and $[0.44, 0.00123, 0, 0, 0, 0.36]^T$. These two scenarios are presented in Sections 3.1 and 3.2 respectively.

We considered the following initial conditions while solving the second version of the problem albeit $[0.44, 0.00123, 0, 0, 0, 0.36]^T$ as in [37] and $[0.437, 0.00123, 0, 0, 0, 0.367]^T$ as used in [40] and [39]. Computational results are discussed and presented with these initial conditions in Sections 3.3 and 3.4. Finally, we used ode15s as the exact solution and compared our errors at $t = 180$ with those of [39] in absolute value sense. Our results outperformed those of [39] which confirms the reliability of our newly developed method for the solution of stiff IVPs.

Furthermore, because the solution of y_4 in Amat et al.'s [37] paper depicts an initial value of $y_4 = 0.007$ and the trajectory of the solutions showed that they used $y_6' = -r_5$ as the last equation. This is what informs the choice of $[0.437, 0.00123, 0, 0.007, 0, 0.367]^T$ as initial conditions and our discussion in Section 3.5 with corresponding tables of comparison made.

3.1 Solution of the Chemical AKZO nobel problem with $[0.44, 0.00123, 0, 0, 0, 0.007]^T$ as initial conditions

According to Amat et al. [37], initially, 0.44 of FBL were mixed with 0.007 of ZUH, but in the course of our numerical computation, it was discovered that with the above initial values the concentration

Table 4: Solution of the AKZO NOBEL problem at $t = 180$ minutes using the new method.

y_i	Amat et al [37]	New method $h = 0.1$	New method $h = 0.01$	New method $h = 0.001$
y_1	0.11493515	0.11426732	0.11426841	0.11426843
y_2	0.00118672	0.00109041	0.00109036	0.00109037
y_3	0.16486622	0.16304979	0.16304932	0.16304932
y_4	0.00331426	0.00036691	0.00036707	0.00036707
y_5	0.16571073	0.02374728	0.02375735	0.02375751
y_6	0.19396618	0.23466433	0.23471397	0.23471475

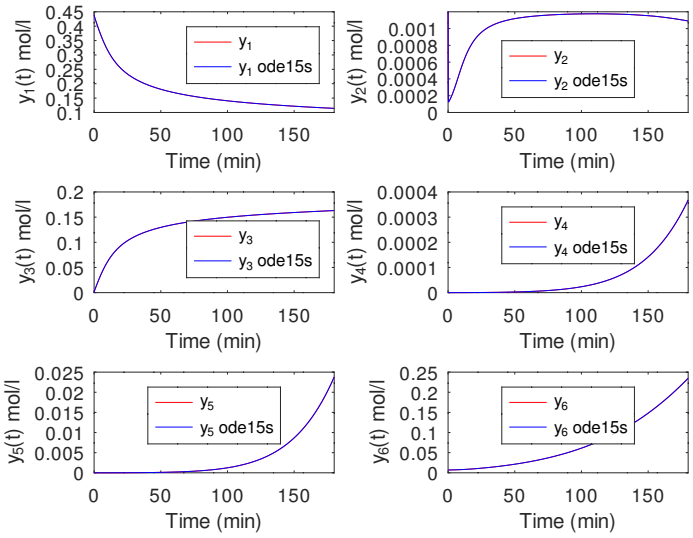

Figure 2: AKZO nobel problem for $h = 0.1$ using the new method on the interval $t \in [0, 180]$.

of FBL.ZUH was zero for all values of t which is impossible. This is what informs the use of the following initial conditions:

$$[y_1(0), y_2(0), y_3(0), y_4(0), y_5(0), y_6(0)]^T = [0.44, 0.00123, 0, 0, 0, 0.007]^T \texttt{mol/liter}.$$

Table 4 shows a comparison of our numerical results with those of Amat et al [37] at $t = 180$. In addition to this, we compared our results with the stiff solver ode15s and these are presented in Figure 2 for $h = 0.1$ and Figure 4 for $h = 0.01$. In Figures 3, 5 and 6, we showed a comparison of our method with ode15s on the interval $[0, 5]$, for $h = 0.1, h = 0.01$ and $h = 0.001$ respectively and our results showed greater promise.

3.2 Solution of the Chemical AKZO nobel problem with $y(0) = [0.44, 0.00123, 0, 0, 0, 0.36]^T$ as initial conditions.

The main aim in this section is to present numerical solution of the chemical AKZO problem, compare our solution to those of ode15s and show some plots of our solution albeit with the initial values $y(0) = [0.44, 0.00123, 0, 0, 0, 0.36]^T$ instead of $y(0) = [0.44, 0.00123, 0, 0, 0, 0.007]^T$ which was used in the last section.

Table 5 shows that our method performed at par with those of ode15s and Figures 7, 8 and 9 further illustrates the strength of the method on the intervals $0 \leq t \leq 180$ and $0 \leq t \leq 5$.

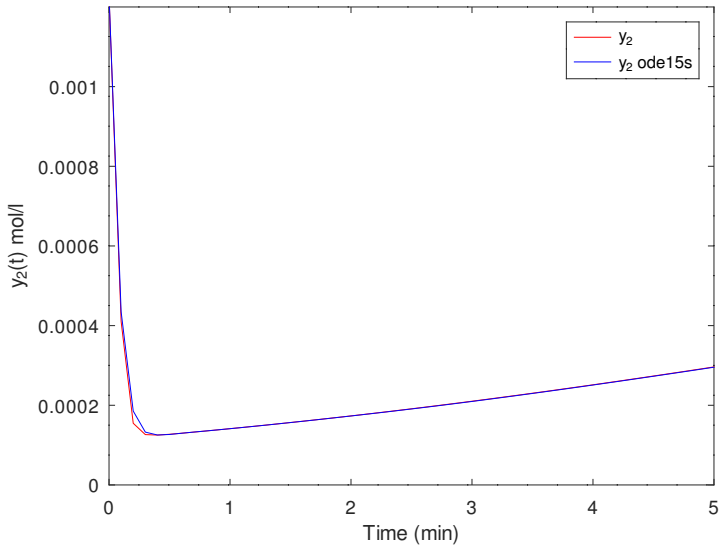

Figure 3: AKZO Nobel problem for $h = 0.1$ using the new method on the interval $0 \leq t \leq 5$.

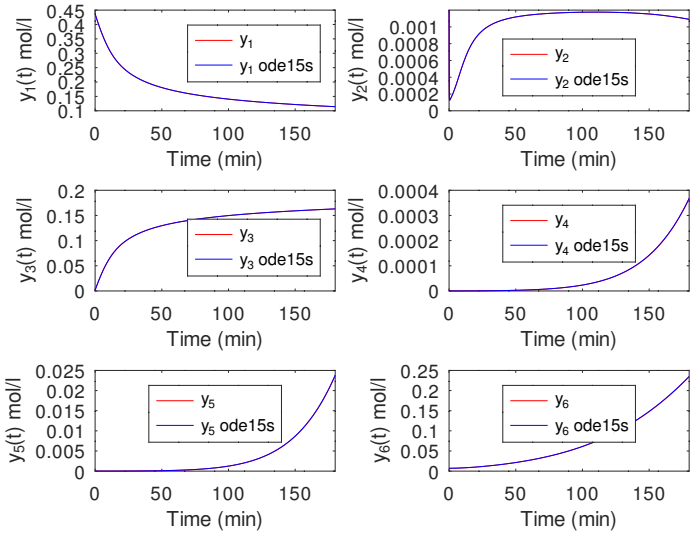

Figure 4: AKZO Nobel problem for $h = 0.01$ using the new method on the interval $0 \leq t \leq 180$.

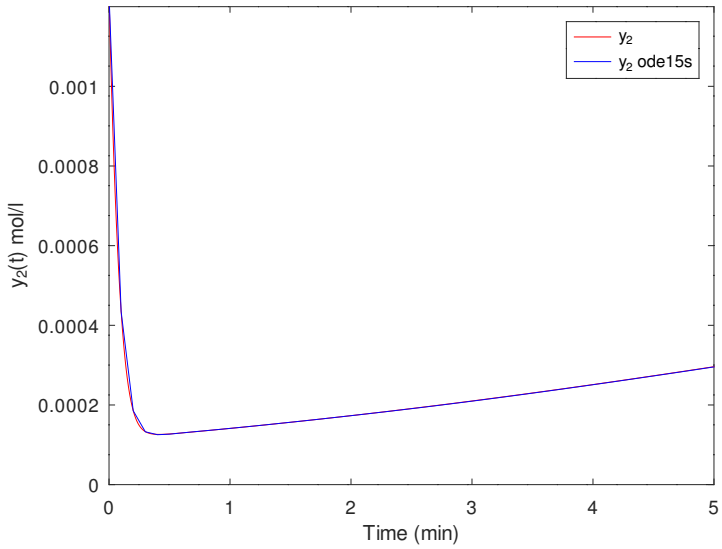

Figure 5: AKZO Nobel problem for $h = 0.01$ using the new method on the interval $0 \leq t \leq 5$.

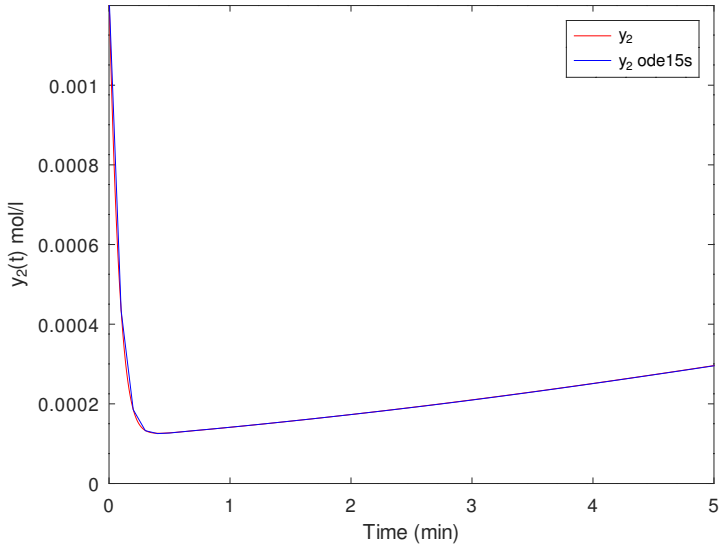

Figure 6: AKZO Nobel problem for $h = 0.001$ using the new method on the interval $0 \leq t \leq 5$.

Table 5: Solution of the AKZO NOBEL problem at $t = 180$ minutes using the new method.

y_i	ode15s	New method $h = 0.1$	New method $h = 0.01$	New method $h = 0.001$
y_1	0.13030558	0.13047147	0.13047551	0.13047561
y_2	0.00012367	0.00012396	0.00012394	0.00012394
y_3	0.16504885	0.16498573	0.16498455	0.16498452
y_4	0.02037300	0.02041253	0.02041420	0.02041424
y_5	0.93651090	0.93707492	0.93711326	0.93711417
y_6	1.23971159	1.23929545	1.23933452	1.23933546

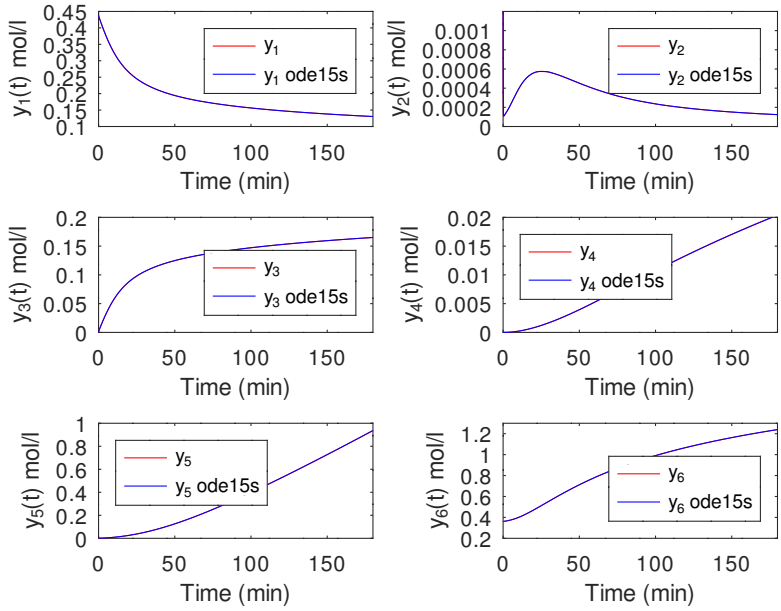

Figure 7: AKZO Nobel problem for $h = 0.1$ using the new first derivative block hybrid method.

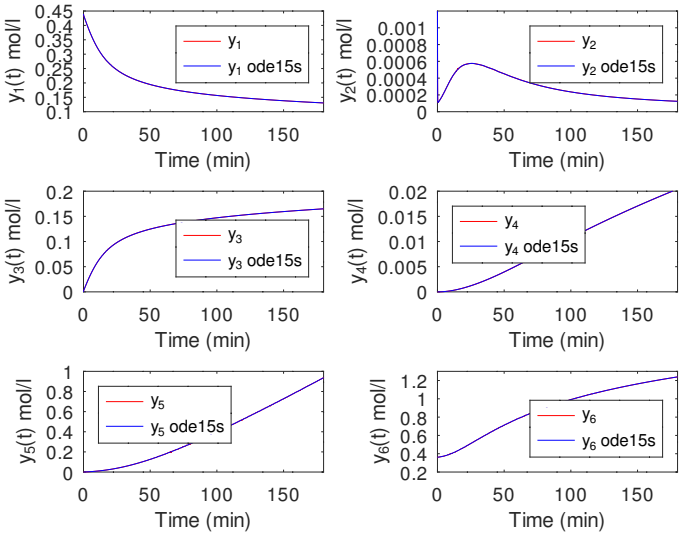

Figure 8: AKZO Nobel problem for $h = 0.001$ using the new method.

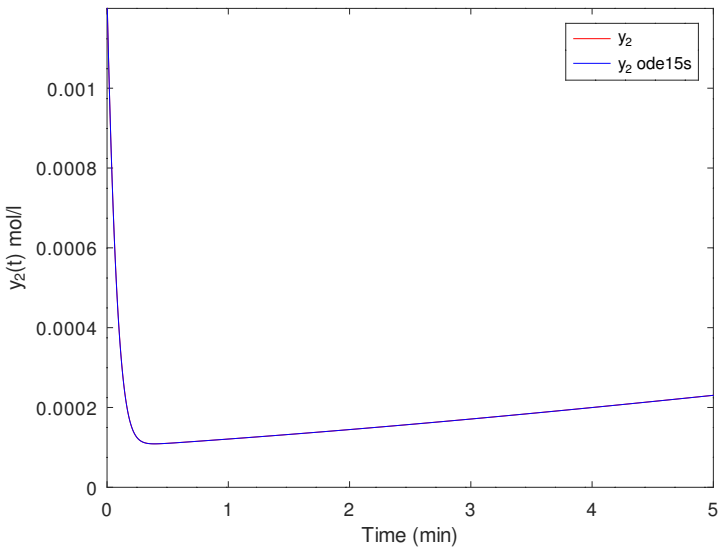

Figure 9: AKZO Nobel problem for $h = 0.001$ using the new method.

Table 6: Solution of the AKZO NOBEL problem at $t = 180$ minutes using the new method.

y_i	Amat et al [37]	New method $h = 0.1$	New method $h = 0.01$	New method $h = 0.001$
y_1	0.11493515	0.11616715	0.11616793	0.11616795
y_2	0.00118672	0.00112122	0.00112122	0.00112122
y_3	0.16486622	0.16355394	0.16355355	0.16355354
y_4	0.00331426	0.00327360	0.00327358	0.00327358
y_5	0.16571073	0.15996171	0.15995924	0.15995919
y_6	0.19396618	0.19676181	0.19676430	0.19676435

3.3 Solution of the AKZO nobel problem when the last differential equation is $y_6' = -r_5$ and $[0.44, 0.00123, 0, 0, 0, 0.36]^T$ [37] as initial conditions

In this section, we replace the last equation of (10) with $y_6' = -r_5$ in line with [40] and [39].

$$\begin{aligned} y_1' &= -2r_1 + r_2 - r_3 - r_4, \\ y_2' &= -\frac{1}{2}r_1 - r_4 - \frac{1}{2}r_5 + F_{in}, \\ y_3' &= r_1 - r_2 + r_3, \\ y_4' &= -r_2 + r_3 - 2r_4, \\ y_5' &= r_2 - r_3 + r_5, \\ y_6' &= -r_5, \end{aligned} \tag{16}$$

we used the following initial conditions $y(0) = [0.44, 0.00123, 0, 0, 0, 0.36]^T$ in line with [37]. The results are as shown in Table 6 and Figures 10, 11, and 12. For all the six concentration variables y_1 to y_6, the solutions obtained using the new method closely match those of the ode15s solver. The close allignment between the curve from the new method and the ode15s results indicates that our method accurately replicates the solution provided by the well established ode15s solver. This suggests that our method is effective and reliable. Figure 13 captured the behaviour of the concentration $y_2(t)$ over time with high precision.

3.4 Solution of the AKZO Nobel Problem when the last differential equation is $y_6' = -r_5$ and $[0.437, 0.00123, 0, 0, 0, 0.367]^T$ [40] as initial conditions.

The focus in this last section is to solve the same version of the AKZO nobel problem as in the last section, but with a different initial condition albeit $[0.437, 0.00123, 0, 0, 0, 0.367]^T$ [40] instead of $[0.44, 0.00123, 0, 0, 0, 0.36]^T$ as initial conditions. It appears that the little approximations in the first and sixth components of the initial conditions will make no difference, but this is proved wrong as shown in Table 7 versus Table 6.

Besides, we compared the absolute errors of our method with those of [39], Table 8 shows the superior accuracy of our method than theirs. Table 9 shows the CPU times for different step sizes for our method in seconds and in minutes.

3.5 Solution of the AKZO Nobel Problem when the last differential equation is $y_6' = -r_5$ and $[0.437, 0.00123, 0, 0.007, 0, 0.367]^T$ [37] as initial conditions.

The main point in this section is to correctly use the right initial conditions in Amat et al's [37] paper and compare the results accordingly. Results of the solution of the chemical Akzo nobel problem with the above initial conditions as well as comparison with [37] is shown in Table 10. We could not make the same comparison in Sections 3.1 and 3.2 as in this section because of the non-consistent initial conditions as well as the difference in the last differential equation. The table shows the superiority and reliability of our method.

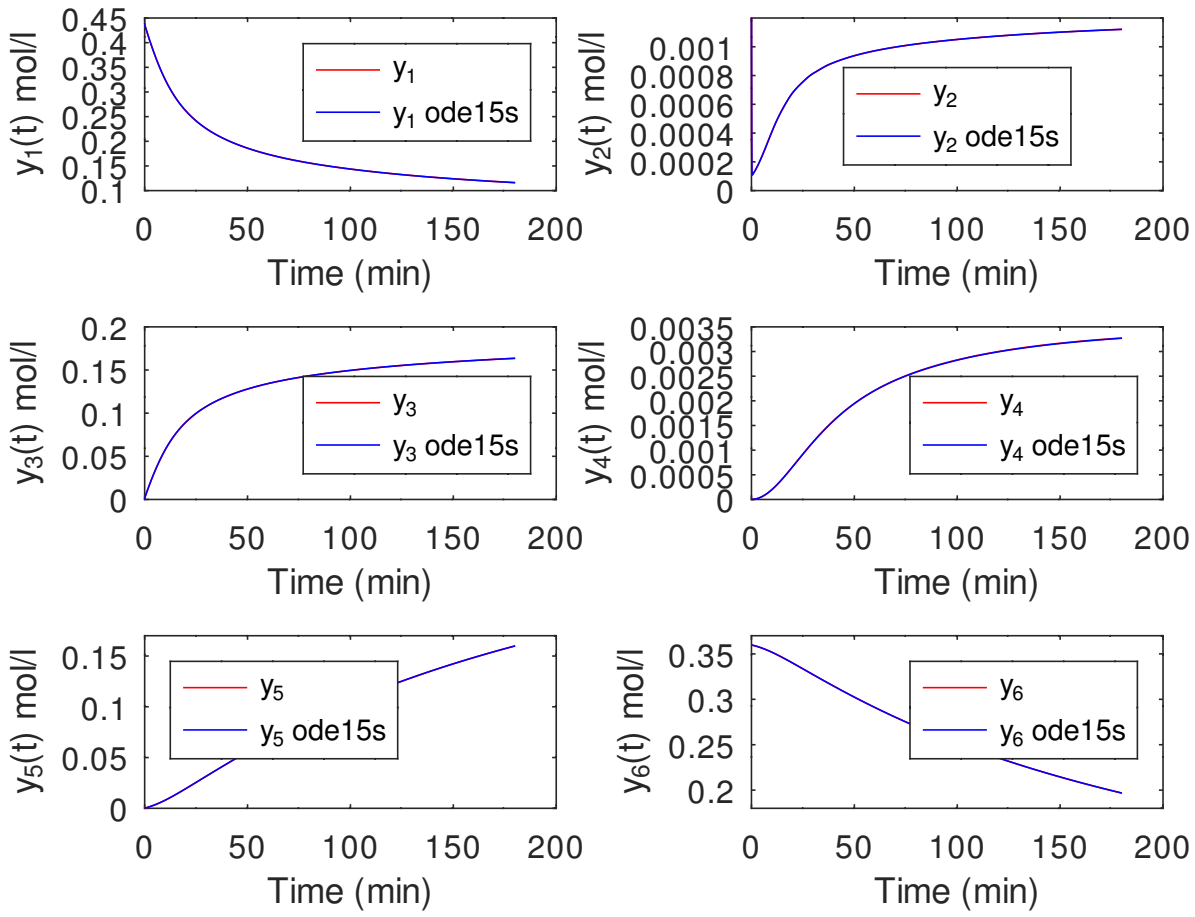

Figure 10: Solution of the chemical AKZO nobel problem with step size $h = 0.1$.

Table 7: Comparison of the solution of the AKZO NOBEL problem at $t = 180$ with `ode15s`.

y_i	`ode15s`	New method $h = 0.1$	New method $h = 0.01$	New method $h = 0.001$
y_1	0.1161498551	0.11618018	0.11618117	0.11618119
y_2	0.0011194263	0.00111944	0.00111944	0.00111944
y_3	0.1621245886	0.16211103	0.16211053	0.16211052
y_4	0.0033974720	0.00340069	0.00340066	0.00340066
y_5	0.1646260981	0.16464670	0.16464367	0.16464362
y_6	0.1989733082	0.19894949	0.19895255	0.19895260

Table 8: Comparison of the solution of the AKZO NOBEL problem at $t = 180$ with [39].

y_i	Absolute Error in [39]	Max absolute Error of our method
y_1	1.16162×10^{-01}	3.13348×10^{-05}
y_2	1.11941×10^{-03}	1.36607×10^{-08}
y_3	1.62125×10^{-01}	1.40686×10^{-05}
y_4	3.39591×10^{-03}	3.21790×10^{-06}
y_5	1.64618×10^{-01}	2.06018×10^{-05}
y_6	1.98954×10^{-01}	2.38189×10^{-05}

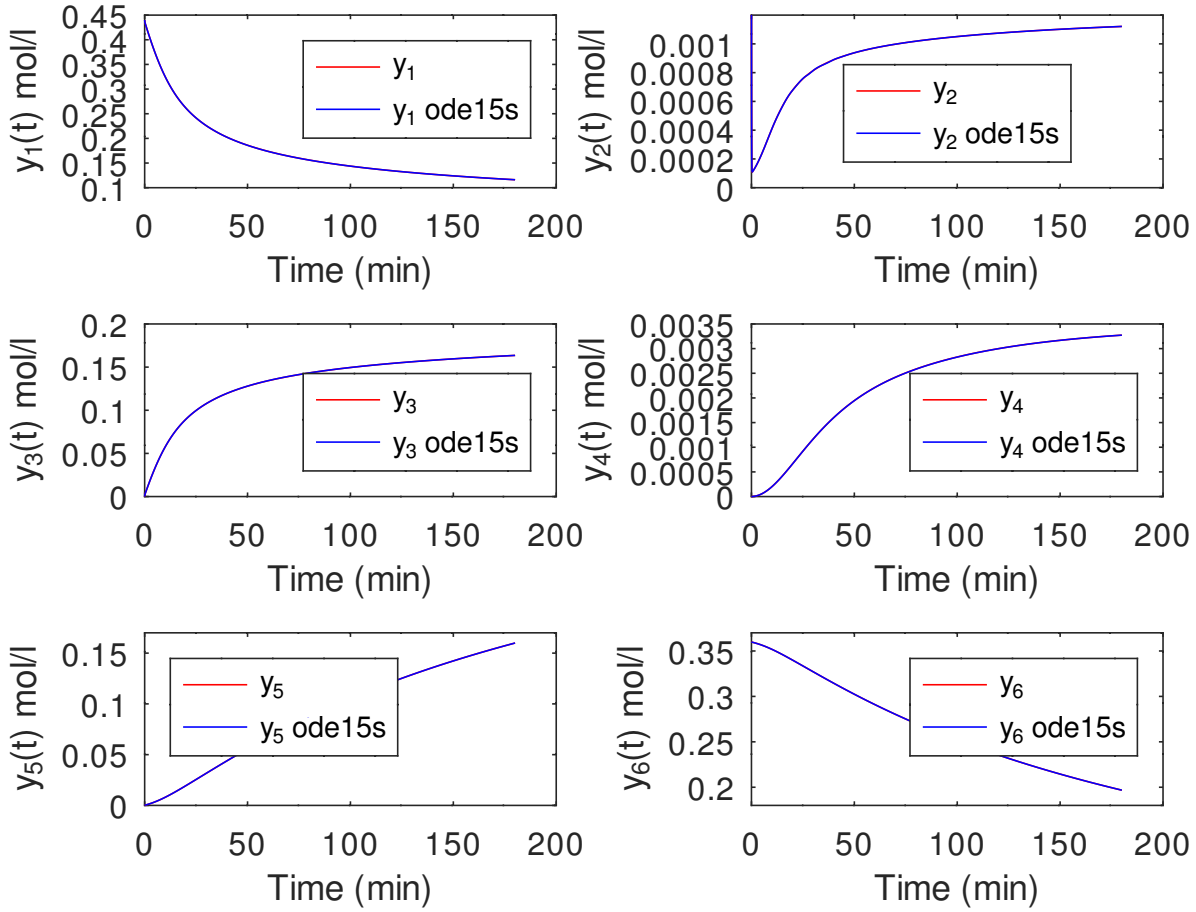

Figure 11: Solution of the chemical AKZO nobel problem with step size of $h = 0.01$.

Table 9: CPU time of the solution of the AKZO NOBEL problem for different step sizes.

CPU time	$h = 0.1$	$h = 0.01$	$h = 0.001$
In seconds	10.1818	152.1100	1816.8000
In Minutes	1.6969	2.5351	3.0280

Table 10: Comparison of the solution of the AKZO NOBEL problem at $t = 180$ with [37].

y_i	Absolute Error in [37]	Absolute Error for $h = 0.1$	Absolute Error for $h = 0.01$	Absolute Error for $h = 0.001$
y_1	1.82735×10^{-03}	6.06282×10^{-05}	5.98382×10^{-05}	5.98182×10^{-05}
y_2	6.59639×10^{-05}	5.39241×10^{-08}	4.39241×10^{-08}	4.39241×10^{-08}
y_3	4.98924×10^{-03}	2.93681×10^{-05}	2.89681×10^{-05}	2.89581×10^{-05}
y_4	1.97534×10^{-04}	1.88430×10^{-06}	1.90430×10^{-06}	1.90430×10^{-06}
y_5	8.69132×10^{-04}	1.03376×10^{-05}	7.86765×10^{-06}	7.80765×10^{-06}
y_6	2.93284×10^{-03}	8.43813×10^{-06}	5.95813×10^{-06}	5.89813×10^{-06}

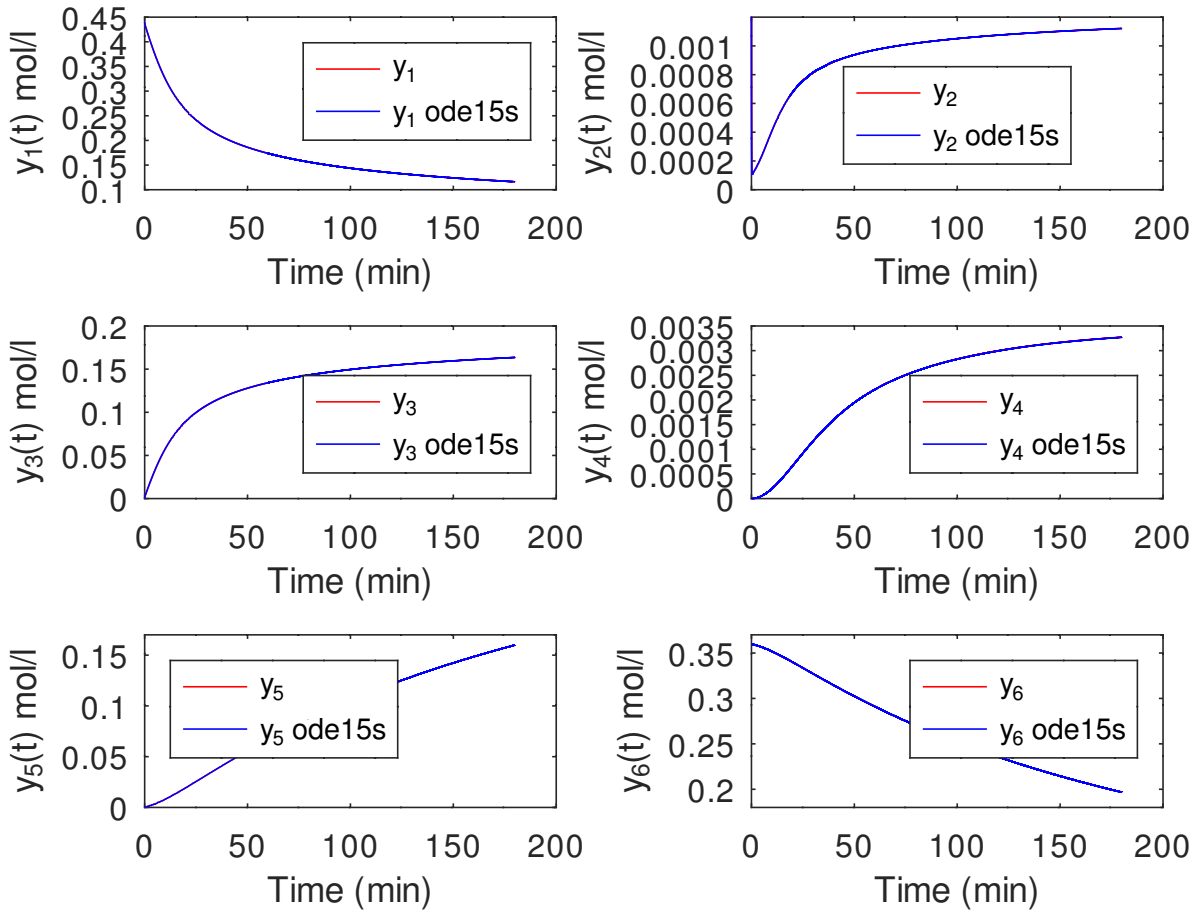

Figure 12: AKZO Nobel problem for $h = 0.001$ using the new method.

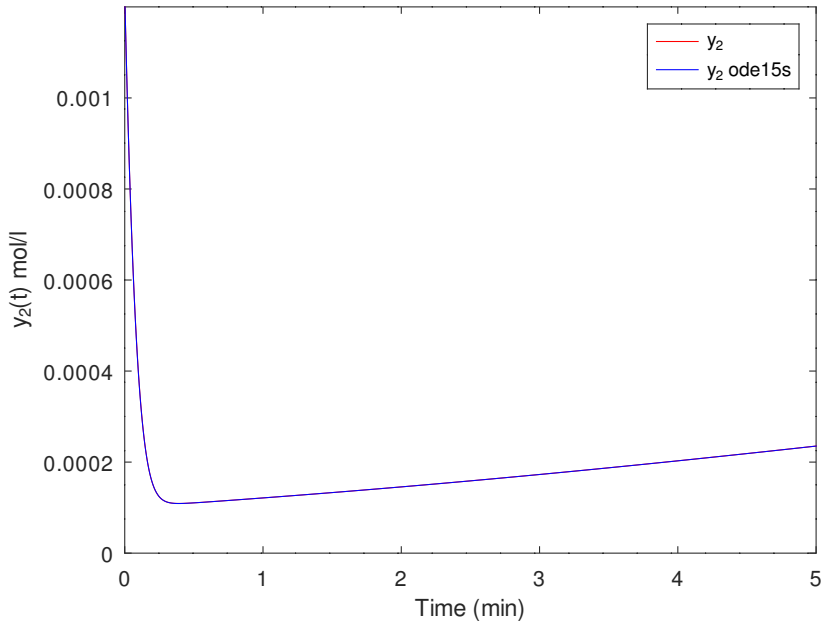

Figure 13: AKZO Nobel problem for $h = 0.001$ using the method. The x-axis represents time in minutes, ranging from zero to five minutes.

4 Discussions and conclusion

In this paper, we have carefully discussed and analyzed the numerical solution of two versions of the chemical Akzo nobel problem using a two–step, self starting block hybrid method which is zero stable, consistent, convergent and A–stable. After comparing the results with the well known stiff solver ode15s, which we used as the exact solution, we discovered that our method gave the minimum absolute error than those of [39] and [37] using the same initial conditions. Therefore, we recommend the new method for the solution of other stiff ODEs because of its improved accuracy.

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