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|---|---|---|
| **To** | : | to whom it may concern |
| **From** | : | Jan Mooiman |
| **Subject** | : | Atmospheric chemistry |
| **Date** | : | 2025-01-14 23:43:45 |

# 1 Atmospheric chemistry

Example taken from Hundsdorfer and Verwer 2003, eq. 1.1, page 7.

We illustrate the mass action law by the following three reactions between oxygen $O_2$, atomic oxygen $O$, nitrogen oxide $NO$, and nitrogen dioxide $NO_2$:

$$NO_2 + h\nu \xrightarrow{k_1} NO + O, \tag{1}$$

$$O + O_2 \xrightarrow{k_2} O_3, \tag{2}$$

$$NO + O_3 \xrightarrow{k_3} O_2 + NO_2. \tag{3}$$

The corresponding ODE system reads

$$\frac{\partial u_1}{\partial t} = k_1 u_3 - k_2 u_1 \tag{4}$$

$$\frac{\partial u_2}{\partial t} = k_1 u_3 - k_3 u_2 u_4 + \sigma_2 \tag{5}$$

$$\frac{\partial u_3}{\partial t} = k_3 u_2 u_4 - k_1 u_3 \tag{6}$$

$$\frac{\partial u_4}{\partial t} = k_2 u_1 - k_3 u_2 u_4 \tag{7}$$

with $\boldsymbol{u}(0) = (0.0, 2.0 \times 10^{-1}, 2.0 \times 10^{-3}, 2.0 \times 10^{-1})^T$ and $\sigma_2 = 10^{-7}$, and the coefficients $k$ are defined as (the given conditions for are different from the conditions as defined in Hundsdorfer and Verwer 2003, page 8):

$$k_1 = \begin{cases} 10^{-5} \exp\left(7\; g(t)\right) \\ 10^{-40}, & \text{during night} \end{cases} \tag{8}$$

$$k_2 = 2.0 \times 10^{-2} \tag{9}$$

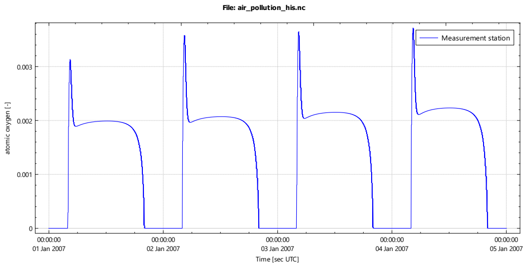
$$k_3 = 1.0 \times 10^{-3} \tag{10}$$

with

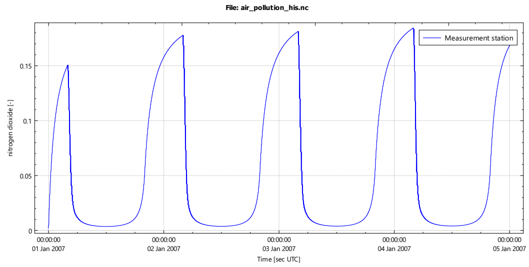
$$g(t) = \left(\sin\left(\frac{\pi}{16}(t_h - 4)\right)\right)^{0.2}, \qquad t_h = \frac{t}{3600}; \tag{11}$$

where $t_h$ is the time in hours.

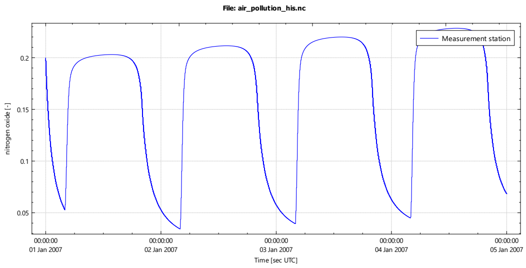
Some results are:



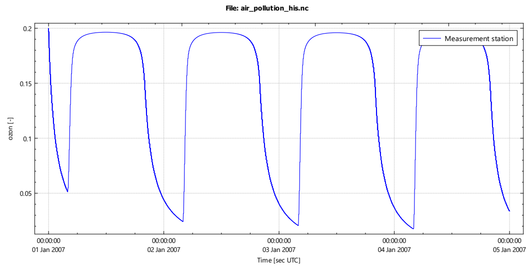

***(a)** Concentration of Atomic Oxygen.*




***(b)** Concentration of Nitrogen Dioxide.*




***(c)** Concentration of Nitrogen Oxide.*




***(d)** Concentration of Ozon.*

***Figure 1:** Result plots of the different constituents, compute with a Runge-Kutta 4 time integration with a timestep of 0.5 [second].*

## 2 Numerics

Discretized

$$\frac{1}{\Delta t}\Delta u_1^{n+1,p+1} = -\frac{1}{\Delta t}(u_1^{n+1,p} - u_1^n) + k_1(u_3^{n+\theta,p+1}) - k_2(u_1^{n+\theta,p+1}) \tag{12}$$

$$\frac{1}{\Delta t}\Delta u_2^{n+1,p+1} = -\frac{1}{\Delta t}(u_2^{n+1,p} - u_2^n) + k_1(u_3^{n+\theta,p+1}) - k_3(u_2^{n+\theta,p+1})(u_4^{n+\theta,p+1}) + \sigma_2 \tag{13}$$

$$\frac{1}{\Delta t}\Delta u_3^{n+1,p+1} = -\frac{1}{\Delta t}(u_3^{n+1,p} - u_3^n) + k_3(u_2^{n+\theta,p+1})(u_4^{n+\theta,p+1}) - k_1(u_3^{n+\theta,p+1}) \tag{14}$$

$$\frac{1}{\Delta t}\Delta u_4^{n+1,p+1} = -\frac{1}{\Delta t}(u_4^{n+1,p} - u_4^n) + k_2(u_1^{n+\theta,p+1}) - k_3(u_2^{n+\theta,p+1})(u_4^{n+\theta,p+1}) \tag{15}$$

Linearization of $\boldsymbol{u}^{n+\theta,p+1}$:

$$\frac{1}{\Delta t}\Delta u_1^{n+1,p+1} = -\frac{1}{\Delta t}(u_1^{n+1,p} - u_1^n) + \tag{16}$$

$$+ k_1(u_3^{n+\theta,p} + \theta\Delta u_3^{n+1,p+1}) - k_2(u_1^{n+\theta,p} + \theta\Delta u_1^{n+1,p+1}) \tag{17}$$

$$\frac{1}{\Delta t}\Delta u_2^{n+1,p+1} = -\frac{1}{\Delta t}(u_2^{n+1,p} - u_2^n) + \tag{18}$$

$$+ k_1(u_3^{n+\theta,p} + \theta\Delta u_3^{n+1,p+1}) - k_3(u_2^{n+\theta,p} + \theta\Delta u_2^{n+1,p+1})(u_4^{n+\theta,p} + \theta\Delta u_4^{n+1,p+1}) + \sigma_2 \tag{19}$$

$$\frac{1}{\Delta t}\Delta u_3^{n+1,p+1} = -\frac{1}{\Delta t}(u_3^{n+1,p} - u_3^n) + \tag{20}$$

$$+ k_3(u_2^{n+\theta,p} + \theta\Delta u_2^{n+1,p+1})(u_4^{n+\theta,p} + \theta\Delta u_4^{n+1,p+1}) - k_1(u_3^{n+\theta,p} + \theta\Delta u_3^{n+1,p+1}) \tag{21}$$

$$\frac{1}{\Delta t}\Delta u_4^{n+1,p+1} = -\frac{1}{\Delta t}(u_4^{n+1,p} - u_4^n) + \tag{22}$$

$$+ k_2(u_1^{n+\theta,p} + \theta\Delta u_1^{n+1,p+1}) - k_3(u_2^{n+\theta,p} + \theta\Delta u_2^{n+1,p+1})(u_4^{n+\theta,p} + \theta\Delta u_4^{n+1,p+1}) \tag{23}$$

Rearrange tp $\mathbf{A}\boldsymbol{x} = \boldsymbol{b}$

$$\frac{1}{\Delta t}\Delta u_1^{n+1,p+1} - k_1\theta\Delta u_3^{n+1,p+1} + k_2\theta\Delta u_1^{n+1,p+1} = \tag{24}$$

$$= -\frac{1}{\Delta t}(u_1^{n+1,p} - u_1^n) + k_1 u_3^{n+\theta,p} - k_2 u_1^{n+\theta,p} \tag{25}$$

$$\frac{1}{\Delta t}\Delta u_2^{n+1,p+1} - k_1\theta\Delta u_3^{n+1,p+1} + k_3\theta u_4^{n+1,p}\Delta u_2^{n+1,p+1} + k_3\theta u_2^{n+1,p}\Delta u_4^{n+1,p+1} = \tag{26}$$

$$= -\frac{1}{\Delta t}(u_2^{n+1,p} - u_2^n) + k_1 u_3^{n+\theta,p} - k_3 u_2^{n+\theta,p} u_4^{n+\theta,p} + \sigma_2 \tag{27}$$

$$\frac{1}{\Delta t}\Delta u_3^{n+1,p+1} - k_3 u_2^{n+\theta,p}\theta\Delta u_4^{n+1,p+1} - k_3 u_4^{n+\theta,p}\theta\Delta u_2^{n+1,p+1} + k_1\theta\Delta u_3^{n+1,p+1} = \tag{28}$$

$$= -\frac{1}{\Delta t}(u_3^{n+1,p} - u_3^n) + k_3 u_2^{n+\theta,p} u_4^{n+\theta,p} - k_1 u_3^{n+\theta,p} \tag{29}$$

$$\frac{1}{\Delta t}\Delta u_4^{n+1,p+1} - k_2\theta\Delta u_1^{n+1,p+1} + k_3 u_2^{n+\theta,p}\theta\Delta u_4^{n+1,p+1} + k_3 u_4^{n+\theta,p}\theta\Delta u_2^{n+1,p+1} = \tag{30}$$

$$= -\frac{1}{\Delta t}(u_4^{n+1,p} - u_4^n) + k_2 u_1^{n+\theta,p} - k_3 u_2^{n+\theta,p} u_4^{n+\theta,p} \tag{31}$$

# 3 Numerical experiment

***Table 1:*** *Stability of different time integrators for the Air Pollution case.*

| | **Time step [s]** | **Euler Explicit** | **Runge-Kutta 4** | **Fully Implicit $\Delta$-formulation** |
|---|---|---|---|---|
| **1** | 0.5 | - | ✓ | - |
| **2** | 60 | ✓ | ✓ | ✓ |
| **3** | 120 | Unstable | ✓ | ✓ |
| **4** | 180 | - | Unstable | ✓ |
| **5** | 240 | - | - | ✓ |
| **6** | 300 | - | - | ✓ |
| **7** | 900 | - | - | ✓ |
| **8** | 1800 | - | - | ✓ |
| **9** | 3600 | - | - | ✓ |

## References

Hundsdorfer, W. and J. G. Verwer (2003). *Numerical solution of Time-Dependent Advection-Diffusion-Reaction Equations*. Springer.