Dear Editor,

We hereby submit a revised version of the manuscript gmd-2016-281 entitled « ASIS v1.0: an adaptive solver for the simulation of atmospheric chemistry » for consideration of publication in GMD. We appreciate the careful and insightful reviews from the anonymous referees. We recall here the response to the comments made by the referees and detail the modifications that we have made in the manuscript. Follows the new version of the article in difference mode that clearly shows the modifications introduced in the revised article.

Best regards,
D. Cariolle

1. Response to general comments

Comment 1a. Accuracy and efficiency of the ASIS solver compared to Rosenbrock’s.

Referee 1. First, from the paper it is not so clear why a new solver is needed. In fact, in the paper there are comments which may make the CTM modeller decide to stick to solvers like Rosenbrock. In particular I would like to see a more detailed comparison against Rosenbrock concerning run time and accuracy, for small and large numbers of chemical species.

Referee 2. It isn’t clear to me though, why such an expensive solver should be preferred over similarly expensive solvers available through
open source packages such as KPP which can provide comparable accuracy and runtimes.

Referee 3. I would also like more discussion of computational cost - the timestep is discussed in detail, but is rarely then compared to the overall run-time. It is certainly interesting to see where the timestep changes, but in terms of usability it would be handy to know exactly how much more time it took.

Response

In section 3 we have discussed in detail the accuracy of the ASIS solver compared to Rosenbrock’s and Gear’s type algorithms. We show that for a given relative tolerance value, Rtol, ASIS has comparable accuracy to those schemes. For low values of Rtol ASIS needs shorter timesteps to maintain comparable accuracy. For the values of Rtol that we believe small enough for atmospheric model simulations (in the range 1 to 3 %), the timesteps of ASIS and those of higher order schemes are comparable, but since ASIS requires less computation the CPU time should be comparable or lower.

We have investigated further this point and we report below several tests performed within the Matlab environment. The following table gives the mean timesteps and CPU time for different box model configurations (the FLUX case of section 3) performed using ASIS and the ode23s code.

<table>
<thead>
<tr>
<th></th>
<th>Rtol</th>
<th>Mean timestep</th>
<th>CPU</th>
</tr>
</thead>
<tbody>
<tr>
<td>ASIS</td>
<td>0,001</td>
<td>4,4</td>
<td>25,5</td>
</tr>
<tr>
<td>ASIS</td>
<td>0,01</td>
<td>23,3</td>
<td>6,4</td>
</tr>
<tr>
<td>ASIS</td>
<td>0,025</td>
<td>49,9</td>
<td>4,8</td>
</tr>
<tr>
<td>Ode23s</td>
<td>0,001</td>
<td>39</td>
<td>58,9</td>
</tr>
<tr>
<td>Ode23s</td>
<td>0,01</td>
<td>44</td>
<td>50,1</td>
</tr>
<tr>
<td>Ode23s</td>
<td>0,025</td>
<td>46</td>
<td>49,9</td>
</tr>
<tr>
<td>Ode23s+J</td>
<td>0,001</td>
<td>39</td>
<td>6,6</td>
</tr>
<tr>
<td>Ode23s+J</td>
<td>0,01</td>
<td>44</td>
<td>6,2</td>
</tr>
<tr>
<td>Ode23s+J</td>
<td>0,025</td>
<td>46</td>
<td>6,1</td>
</tr>
</tbody>
</table>

If ode23s is used without providing a subroutine for the computation of the Jacobian of the chemical system the ode23s code is much slower than ASIS, by a factor 2 to 10. This is because the ode23s code computes by differentiation an approximation of the Jacobian. It requires
more iterations with the subroutine that computes the chemical tendencies and the CPU cost is rather high. If the routine that computes the Jacobian is provided to ode23s, the CPU cost decreases significantly (lines Ode23+J of the table) and becomes comparable to the CPU used by ASIS. At low tolerance ode23s+J is faster than ASIS, at higher tolerance the costs of ASIS and ode23s+J are comparable.

The important point to mention is that within the Matlab environment the CPU cost does not come from the linear algebra parts of the algorithms but from the evaluation of tendencies and Jacobian matrices. Therefore it is very dependant upon the chemical system and the details of the programming of the associated subroutines.

The situation is quite different within the Fortran environment. With the Fortran version of ASIS the CPU cost for the calculation of the Jacobian (the matrix M of eq. 7) is negligible compared to the linear algebra computations. This is because the compiler handles efficiently the associated subroutine (fill_matrix) that contains frequent indirect addressing. It is not possible to evaluate if this is also the case with all the codes based on Rosenbrock’s algorithm, but if it is so ASIS should perform well when the mean time steps are comparable since it needs less linear algebra computations.

In conclusion we cannot give a general statement on the computational cost of ASIS compared to Rosenbrock’s solvers. It is too dependant on the computational environment, on the details of the coding of the tendencies and the Jacobian matrices associated with the chemical scheme, and on the chemical scheme itself in particular the number of species and its stiffness.

Our objective is to offer an alternative to existing solvers having in mind that ASIS should be rather effective at the rather high tolerance error that can be used by most atmospheric models. Its formulation is not complex so it can be easily coded within the environment of existing models with the help of the example available on line (see the following comment 1.d). Our approach is to avoid the use of external pre-processors that are often judged not user-friendly by modellers because the generated code has to be adapted to the chemical models (see discussion in section 7).

It is clear that if a modeller uses already an implementation of a Rosenbrock solver like KPP, the effort to turn to ASIS might be too high compared to the expected benefit. But many models do not use solvers based on Rosenbrock’s or Gear’s methods and we believe that ASIS could be an interesting and simple alternative for them.
Change in the manuscript:
In section 3.4 we have extended the table 4 to introduce the results of the simulations discussed above. In particular the ratio of CPU relative to the R1 simulation is given.
In addition we have introduced in the same section (page 11 and 12, from lines 284 to 297) a detailed discussion of the performances of ASIS relative to the Rosenbrock ode23s code.

Comment 1b. References of other solvers

Referee 1. There are no references given in the introduction to the general literature on chemical or differential equation solvers. An introduction should sketch the starting point of the work - the state-of-the-art - and in this way clarify how the new developments described in the paper advance this present knowledge and models. I suggest that the authors add a section with references discussing the current status concerning solvers in relation to chemistry models. Several references are provided later on in the paper, but the current list is not very extended and could be expanded somewhat.

Response:
The references to existing algorithms, solvers, and their use by chemical models are given in section 2 in connection to the discussion of the numerical treatment of the species tendency equations. By doing so we believe that the reader better sees which class of solver is associated with a given treatment of the equations. In the manuscript we give reference to the most widely used explicit (CHEMEQ, TOWSTEP, QSSA) and implicit (SIS, Rosenbrok’s and Gear’s) schemes.
Our objective is not to make an exhaustive review article on numerical methods and solvers but to illustrate the specificity of our scheme compared to existing solvers.

Change in the manuscript:
In the introduction (page 2, from lines 34 to 40) we have introduced references to the main class of solvers, implicit versus explicit, and multi-step versus one-step algorithms.
In section 2.1 additional references to chemical models and their associated solvers have been added (page 4, lines 99, 103, 104).

Comment 1c. Duration of the numerical simulations

Referee 2. I find it a shame that only 3 month simulations are performed with the global models using the ASIS scheme. It would be very
interesting to know what effect the replacement of the chemical solver would have on many other features of global atmospheric chemistry, such as the global oxidising capacity and related aspects such as the methane lifetime and tropospheric ozone budget.

Referee 3. The run length is also a bit short for most cases. The 1 day simulations for the box model are very short, especially when it appears that the A2 case is diverging from the R1/G1/A1 cases. Have these simulations been run for longer, and if so, how do the results of A2 (& A3) evolve? Also, A3 is not plotted at all, but these settings are then used for the MOCAGE simulations. The A3 results should also be included in the plots in Figures 1 & 2 (or plotted separately with a larger scale if required).

The GCM lengths are slightly better (3 months and 150 days), but still short. Are there plans to do longer runs with a full evaluation and budget analysis? The results presented here have highlighted deficiencies in the existing models, but a full analysis on longer simulations would be required to properly validate ASIS, as opposed to this paper which describes its implementation.

Response:
The objective of the reported simulations is to present the characteristics of the ASIS solver in terms of accuracy and adaptability to various chemical schemes and situations.

The 1-day simulation with the box model is long enough to evaluate the accuracy of the solver. We have extended the simulations up to 3 days for the FLUX case and the results obtained are fully consistent with the 1-day simulation. The next figures show for example results of the time evolution of O₃ and NO₂ concentrations in a 3-day extension of the A3 experiment (with the largest tolerance, 0.025) and its relative difference with an extended G1 experiment.
As can be seen there is no specific trend in relative differences between the species, the differences remain in the range of the chosen relative tolerance. In the revised manuscript we will include in figure 1 the results of experiment A3.

The 3D simulations illustrate the benefit of using a solver like ASIS that has a controlled accuracy and is mass conserving. The 3-month simulation with MOCAGE is short, but long enough to point out the benefits from the ASIS use. We agree that a more fully validation of MOCAGE+ASIS would require longer simulations, in particular to assess the impact of ASIS on the longer-lived species. This is however beyond the scope of this article. Multiyear simulations of MOCAGE+ASIS are planned in the near future along with simulation of the C-IFS model (Flemming et al., 2015) with the RACMOBUS chemical scheme.

**Change in the manuscript:**
We have included the results of experiment A3 in the figures 1 and 2.

**Comment 1d. Code availability**

Referee 1. - p29, code availability: “The ASIS code is property of the CERFACS and includes libraries that belong to other holders.” Does this imply any restrictions if other parties want to use the code? Is there a kind of license for using the code?

Referee 2. If the authors do not seriously intend to make their code generally available to the community, and are content with limiting its use to in-house applications, differentiating their product from other alternatives in this way is arguably outside the scope of the manuscript.

**Response:**
After discussions with the holders of the different parts of the code it was agreed that the 0D Fortran code used in section 3 will be made generally available on the CERFACS’s server.

**Change in the manuscript:**
In section 7 (page 30, lines 569 to 570) we give indication on how to obtain a copy of the Fortran code: as a supplementary file to the article or on the CERFACS server.

**Comment 1e. Synthesis of the simulations**

*Referee 3.* Due to the large number of tests performed it was a little difficult to keep track of the settings used in each case. I would recommend giving a master table (or tables) giving the configuration for each shorthand used in the plots (e.g. R1, G1, A1, A2, A3, A4, MR, MA, EB, ASIS etc.) and what the settings are used for each (e.g. values for ATOL, RTOL, using ode23s, ode15s, DGESV, GS, GMRES etc.), the experiment run (e.g. FLUX, STRATO, MOCAGE, Mars Box Model, LMD Mars GCM etc.), and also the chemistry scheme used (e.g. RACMOBUS, Mars). This would be especially helpful for comparing between sections, as it can be difficult to pick out this mass of information from the text.

**Response:**
We will extend table 4 to give the information required by Referee 3.

**Change in the manuscript:**
The table 4 has been extended to include a summary of the input/output of the simulations for the FLUX case.
For the STRATO case the name of the simulation was change to mirror the name used for the FLUX cases: AS2 of the STRATO refers to the A2 simulation of the FLUX case using the same settings for ASIS.

**2. Response to specific comments**

The typos and english shortcomings have been addressed in the revised manuscript and are not detailed hereafter.

Equally, we will improve the quality of the figures as suggested by referee 3.

**Change in the manuscript:**
Some figures have been redrawn to increase their quality. One figure was deleted (figure 3 of the original manuscript) in order to shorten the
article and because its content was not essential for the understanding of the model results.

**Comment by Referee 3.** p2 line 30: I'm confused by "It is also desirable to let to the user a minimum of free parameters to tune". Do you mean "desirable to give the user"?

**Response:**
Yes, the idea is to give to the user a choice in a limited number of parameters that control the accuracy of the solution.

**Change in the manuscript:**
The sentence has been changed (page 3 line 59).

**Comment by Referee 1.** p3, line 25: The second term on the left is diagonal. Please explain why? Diagonal in which space?

**Response:**
L(t, C) being completely explicit, the matrix (I + L(t, C) δt) is diagonal by construction.

**Change in the manuscript:**
The sentence has been changed (page 4 line 90).

**Comment by Referee 1.** p3, line 27: “mass conservation is not maintained”. Can you add a reference or text book? Is it possible to describe in one line how the reader may understand that there is no conservation of mass?

**Response:**
The mass conservation is not maintained when the species tendencies associated to a given reaction are different after time discretisation. This is for instance the case with the simple BDF scheme. We will recall this in the revised manuscript.

**Change in the manuscript:**
The sentence “The mass conservation is however not maintained due to the fact that for a given reaction between two species the value of the associated tendency is different for each species.” is added page 4 line 92.

**Comment by Referee 3.** p4 line 18: I think you mean "Sandu and Sander (2006)", although I can’t find this reference in the reference list. I assume it is Sandu, A. and Sander, R.: Technical note: Simulating chemical systems in Fortran90 and Matlab with the Kinetic PreProcessor KPP-2.1, Atmos. Chem. Phys., 6, 187-195, doi:10.5194/acp-6-187-2006, 2006. I haven’t gone through and double-checked all the other references, but I suggest that the authors do so.

**Response:**
Yes this is the right reference. We will double-check again all the other references.

**Change in the manuscript:**
The reference has been added (page 33 line 673).

**Comment by Referee 1.** p5, line 27: Why is beta >= 1 required? Should this be beta > 0?

**Response:**
Beta > 0 is enough from a mathematical point of view, but to better discriminate between implicit and explicit parts for the species tendencies beta >1 is more appropriate. We have tested values for beta >1 but not investigated 0 < beta < 1.

**Change in the manuscript:**
This point is briefly discussed in the revised manuscript (page 6, line 164)

**Comment by Referee 1.**- Fig.6. The colour scale is unclear: Does the colour between 1 and 2 mean there are two substeps or one substep? I assume “number of sub-timesteps” can only take integer values.

**Response:**
The first colour (dark blue) corresponds to 1 sub-timestep. The colour scale intervals should be read [lower value, higher value].
The number of sub-timesteps can of course only take integer values. However we show interpolated values from model levels (which are function of ground pressure) to pressure levels (50hPa and 540hPa) and interpolated values are generally not integers.

**Comment by Referee 3.** p22 line 1: Do you mean "4.7 times"? Is this a mean over the whole 3-month run?

**Response:**
Yes it is 4.7 times, calculated over the 3-month run.

**Change in the manuscript:**
It is now specified “4.7 times” in the revised manuscript (page 22 line 427).

**Comment by Referee 1.** p25, line 32: “4 times smaller”. How can I see this from the figure 12, which has a scale ranging between -30 to 30%?

**Response:**
In order to highlight differences obtained during the day, the colour scale of Figure 12 is limited to maximum and minimum values of ±30%. This is now mentioned in the legend. The related text in the body of the manuscript will be modified as follows:
“Regarding OH, the GCM results confirm the poor description of the HOx chemistry by the EB scheme at the terminators. At night, OH values calculated by EB are more than 30% smaller than with ASIS”.

**Change in the manuscript:**
The sentence has been rephrased “At night, OH values calculated by EB are more than 30% smaller than with ASIS” (page 27, line 521).

**Comment by Referee 3**
p26 Figure 11: When is this from - is it a snapshot from the start/middle/end of the 150-day run?

**Response:**
It is a snapshot at the end of the 150-day run, now indicated in the revised legend of Figure 11.

**Change in the manuscript:**
The legend has been changed for what is now figure 10.

**Comment by Referee 3**
page 27 Figure 12: Similarly for Figure 11 - when is this from with respect to the start of the run. Is it the same as for Figure 11?

**Response:**
Yes similarly to Figure 11 this is a snapshot at the end of the 150-day run. This will be indicated in the revised legend of Figure 12.

**Change in the manuscript:**
The legend has been changed for what is now figure 11.

**Comment by Referee 1**. p28: I was wondering if ASIS could be used for adjoint (4D-Var) type of applications?

**Response:**
In theory, the adjoint of the ASIS code can be developed. It requires that all the intermediate calculations (sub-timesteps, matrix M evaluations, ...) be stored. Then the adjoint of the successive linear operators can be derived if a direct method (for instance based on a LU decomposition) is used to solve the linear systems (eq. 7). The situation is more complex if an iterative solver is used.

However we do not plan to develop the adjoint of the ASIS code, we are alternatively exploring ensemble methods (Emili et al., 2016) for assimilation applications.

**Change in the manuscript:**
No change has been made; this subject is out of the scope of the article (but of interest for the referee).

References

ASIS v1.0: an adaptive solver for the simulation of atmospheric chemistry

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Abstract. This article reports on the development and tests of the Adaptive Semi-Implicit Scheme (ASIS) solver for the simulation of atmospheric chemistry. To solve the Ordinary Differential Equation systems associated with the time evolution of the species concentrations, ASIS adopts a one step linearized implicit scheme with specific treatments of the Jacobian of the chemical fluxes. It conserves mass and has a time stepping module to control the accuracy of the numerical solution. In idealized box model simulations ASIS gives results similar to the higher order implicit schemes derived from the Rosenbrock’s and Gear’s methods and requires less computation and run time at the moderate precision required for atmospheric applications. When implemented in the MOCAGE CTM and the LMD Mars GCM the ASIS solver performs well and reveals weaknesses and limitations of the original semi-implicit solvers used by these two models. ASIS can be easily adapted to various chemical schemes and further developments are foreseen to increase its computational efficiency, and to include the computation of the concentrations of the species in aqueous phase in addition to gas phase chemistry.

1 Introduction

In Chemical Transport Models (CTMs) or General Circulation Models (GCMs) the description of atmospheric chemistry has rapidly increased in complexity. Early model developments were devoted to the study of the stratospheric and upper tropospheric compositions focussing on the gas phase reactions that control the ozone distribution. Emphasis has afterwards been put on tropospheric chemistry due to its oxidant properties and its possible impact on climate via the lifetime of several greenhouse gases and the distribution of secondary-formed aerosols.

Large scale models include chemical schemes that deal with about hundred species and several hundreds of reactions in gas-phase and in heterogeneous phases (solid and liquid). Most of those species undergo transport processes, like advection, diffusion and convection. As a result the models include the resolution of complex coupled systems which cannot be handled in a single operator. In practice the various processes are decomposed in a series of operators that are solved numerically in sequence. For example the time evolution of the species are first calculated taking into
account advection, then diffusion, convection, and so on. Among these processes the evolution of the species due to chemical
transformations is a key component of the models.

The models have to solve coupled ODE—Ordinary Differential Equation (ODE) systems that describe the adopted chemical
mechanism. These ODE systems are of the non-linear form:

\[ \frac{\partial C}{\partial t} = f(t,C) = P(t,C) - L(t,C).C \]  

(1)

where \( C \) represents the vector of the local species concentrations, \( P(t,C) \) and \( L(t,C) \) the production and loss term matrices.
The stiffness of the systems comes from the wide range of values that can take the production and loss terms. Small values of
the loss term correspond to stable species having long lifetimes (e.g. CH₄, N₂O, ...) whereas large values correspond to radical
species (e.g. O(^1D), OH, Cl, ...) with short lifetimes. Typical atmospheric situations lead to species lifetimes ranging from
milliseconds to years. Since the other physical processes can change the conditions and compositions of the air masses (i.e.
surface emissions, transport at all scales, day-night transitions, etc...) the chemical system is often out of chemical equilibrium
and the ODE system to be solved can be very stiff.

Adequate algorithms must then be used for its resolution to deal with the stiffness of the ODE systems and to achieve good
accuracy. Existing algorithms vary in formulation and complexity. They can be classified has explicit or implicit schemes (see
e.g. Sandu et al., 1997a), and use single or multistep or multistage methods (Sandu et al., 1997b). Multistage implicit algorithms
based on Gear (Hindmarsh, 1980) and Rosenbrock (Hairer and Wanner, 1991) formulations are the most accurate but require
a significant amount of computation, which limits their use in comprehensive atmospheric chemistry models. To reduce the
computational cost the solver described in the present article is based on a one-step implicit algorithm. Its characteristics are
detailed in the next sections along with comparisons with other implicit schemes.

For atmospheric applications some numerical properties of those algorithms should be particularly sought for:

i) Mass conservation—: Atmospheric models are often integrated for long term simulations, up to several decades for global
climate simulations, and small trends and anomalies are investigated. Any bias or trend in the atmospheric composition due
to numerical algorithms must therefore be avoided. It is therefore essential that the algorithms chosen to solve the chemical
systems preserve mass. All the atoms or elementary groups of atoms (e.g. nitrogen oxides) must be conserved.

ii) Accuracy—: It is of course always desirable to obtain a numerical solution as accurate as possible, although the uncertain-
ties associated with the other operators and the fact that they are integrated successively in time introduce a significant degree of inaccuracy. This leads also to transient evolutions in the chemical system, especially for the short lived radicals, that have no real physical basis. It is not always necessary to obtain a very accurate numerical solution during those transient evolutions if they do not last long and have little impact on the solutions for the other longer lived species. The key point is to design an algorithm where the accuracy can be chosen a priori by the user and controlled during the course of the numerical integration.

iii) Positivity—: It is highly desirable to maintain positivity of the concentrations. Otherwise instability might arise when
coupled to other operators dealing with advection or convection of the minor species. Some algorithms maintain positivity
of the solution by construction, others introduce clipping of the negative values at the expense of local mass conservation.
Negative values can be tolerated if they are small and transient, and if they have little impact on the algorithms used to account for the other physical processes.

iv) Adaptability and flexibility. The adopted solver should cope with a variety of chemical mechanisms with the possibility to easily add or remove species and reactions. It is also desirable to let give to the user a minimum of free parameters to tune.

The solver should also run efficiently on a large variety of computers without having to rewrite large parts of the code. This can be obtained with extensive use of mathematical libraries that are often optimized for the computer being used.

This article describes a solver for the simulation of gas-phase atmospheric chemistry, the Adaptive Semi-Implicit Scheme (ASIS), that has most of the desirable properties discussed above. Section 2 gives the basic formulation of the scheme and discusses its characteristics in comparison with other solvers currently used within atmospheric models. Section 3 gives results from box-model simulations and comparison box-model simulations and comparisons with other state of the art algorithms, and sections 4 and 5 detail the implementation of ASIS within the MOCAGE CTM (Michou et al. and Peuch, 2002; Josse at al., 2004; Teyssèdre et al., 2007) and the GCM of planet Mars (Lefèvre et al., 2004) of the Laboratoire de Météorologie Dynamique (LMD). Possible future extensions of the solver are discussed in the last section.

2 ASIS: description of the chemical solver

2.1 Implicit discretisation and numerical methods

The integration of Eq. (1) cannot be done using a simple one-step explicit scheme with the left-hand side terms evaluated at time t, as numerical stability would required to use timesteps lower than the shortest species lifetime. Since some radicals have lifetimes lower than a few milliseconds in the atmosphere too many iterations would be required to obtain simulations for hundred or more days with affordable computer time. Several explicit methods have been developed to address this issue which are based on classification of the species according to their lifetimes. For instance with the QSSA method (Hesstvedt et al., 1978) the fast species with lifetimes much lower than the timestep are often assumed to be at equilibrium, $C = P/L$, the intermediate species are obtained using an exponential solution of Eq. (1) and the long-lived species are computed using the simple explicit solution. Other explicit schemes gain in accuracy with the use of multi-step algorithms with predictor-corrector evaluations of the concentration at time $t + \delta t$. For instance the CHEMEQ solver of Young and Boris (1997) with subsequent developments by Mott et al. (2001, 2000). Limitations of these explicit schemes are that they often do not conserve mass and that the choice of species classifications is somewhat arbitrary. Mass conservation can be improved using the technique of "species lumping" where additional equations are introduced for linear combinations of species concentrations to reduce the stiffness or enforce conservation for a chemical family. The drawback of those approaches is that the algorithm becomes problem dependent and requires a very good knowledge of the chemical system especially when updating the constant rates or the list of reacting species.
One possibility to increase the timestep is to treat part of the right-hand side of Eq. (1) implicitly, for instance keeping the evaluations of P and L at time \( t \) but C at time \( t + \delta t \):

\[
C^{t+1}(I + L(t,C)\delta t) = C^t + P(t,C)\delta t
\]

(2)

where \( C^{t+1} \) is the concentration vector of the species at time \( t + \delta t \). The second term of the left hand side of this equation is diagonal so its numerical resolution forms a diagonal matrix so the numerical solution of Eq. (2) is straightforward.

With this discretisation the numerical solution is positive and unconditionally stable. The mass conservation is not maintained, however not maintained due to the fact that for a given reaction between two species the value of the associated tendency is different for each species.

One way to alleviate this problem is to discretize Eq. (2) fully implicitly in time using the simple backward Euler (EB) method:

\[
C^{t+1}(I + L(t+1,C)\delta t) = C^t + P(t+1,C)\delta t
\]

(3)

Resolution Solution of Eq. (3) requires an evaluation of the terms \( L(t+1,C) \) and \( P(t+1,C) \) that can be obtained using \( C^{t+1} \) from the resolution solution of Eq. (2). In practice Eq. (3) is solved iteratively with successive evaluations of \( C^{t+1} \), for instance using the iterative Newton method. A correcting term to the iterative solution can be also added to increase the accuracy (Stott and Harwood, 1993; Carver and Stott, 2000). Still, the mass conservation can only be obtained if a good convergence of the solution is reached and additional constraints such as species lumping or equilibrium assumptions for the shorter lived species are often used to increase accuracy and to speed up convergence. A scheme of this type is are for example used within the MOZART model (Emmons et al., 2010), the ECHAM-HAMMOZ model (Pozzoli et al., 2008), the TM5 model (Huijnen et al., 2010), the UKCA climate-composition model (O’Connor et al., 2014) and the MOCAGE CTM.

The implicit methods described above to solve the ODE chemical system are all one timestep: only concentrations at time \( t \) are used to evaluate the concentrations at time \( t + \delta t \). Although the numerical stiff ODE field is largely developed and precise accurate ODE solvers are available and have been used for atmospheric chemistry problems, many of them are multi-steps or multi-stages. Consequently, several evaluations of \( C \) at various past or intermediate timesteps are used to obtain the concentration at time \( t + \delta t \). A direct extension of the simple backward Euler method is to use higher order backward differentiation formula (BDF) to solve Eq.(1). Based on that approach Verwer (1994) has developed the TWOSTEP atmospheric chemical solver, which uses a second order BDF formula combined with a Gauss-Seidel iteration technique to solve the resulting implicit system. This solver can be very efficient but it is not naturally mass conserving. It is for example implemented in the CHIMERE model (Menut et al., 2013).

Mass conserving, multi-step or multi-stage and high order accurate implicit methods exist to solve the ODE stiff system. Among the methods based on BDF, Gear’s predictor-corrector method has been adapted to atmospheric chemical systems, for example the SMVGAR code (Jacobson and Turco, 1994) implemented in the GEOSCHEM CTM (Bey et al., 2001). More recently the Rosenbrock’s method (Rosenbrock, 1963), is becoming widely used in atmospheric chemistry modelling (Sandu et al., 1992, 1997b) despite the fact that its computational cost is still rather high compared to approaches based on low order
BDF methods. The implementation in chemical models of Rosenbrock’s and other high-order methods has been eased by the development of the Kinetic PreProcessor (KPP) by Sandu et al. and Sander (2006), which allows the choice of an integration method and generates the adequate codes accordingly.

When the chemical scheme involves more than a hundred species and over two hundreds of reactions, the implicit multi-stage methods are still computationally expensive, especially if they are to be used within global 3D models with horizontal resolutions of the order of $1^\circ \times 1^\circ$, with several tens of vertical levels and for simulations lasting for several years. The increase of the computational cost comes from the need to solve at each stage a linear system of the order of the number of species, and this cost varies non-linearly (often quadratically, see for example Golub and Van Loan, 2013) with the number of species.

### 2.2 Formulation of the ASIS solver

The approach adopted for ASIS is to restrict the algorithm to a single implicit step combined with a specific evaluation of the Jacobian matrix of the chemical fluxes, $J = f'(C) = \partial f / \partial C$.

The starting point comes from the decomposition of chemical tendencies in three terms:

$$\frac{\partial C_k}{\partial t} = \sum_{l,m} \sigma K_{l,m} C_l C_m - D_k C_k + F_k$$  \hspace{1cm} (4)

with $\sigma = -1$ if $m = k$ and $l \neq k$, $\sigma = -2$ if $l = m = k$, and $\sigma = 1$ if $l$ and $m \neq k$, where $C_k$ is the concentration of the $k$ species.

The first term of the right-hand side corresponds to the chemical productions or destructions due to first order reaction rates with constants $K$. The second term arises from thermal decompositions and/or photodissociations of species with a rate $D$, and the last term accounts for external tendencies that come from other physical processes than chemistry. For example the surface emissions affecting the lowest levels of the model will result in species tendencies $F$.

The time discretization of Eq. (4) is then performed with a semi-implicit scheme for the first term adapted to each reaction and timestep, an implicit discretization for the second one and the external tendencies are assumed to be constant over the timestep $\delta t$:

$$\frac{(C^{t+1}_k - C^t_k)}{\delta t} = \sum_{l,m} \sigma K_{l,m} [\Delta^t_{l,m} C_l^{t+1} C_m^t + (1 - \Delta^t_{l,m}) C_l^{t+1} C_m^t] - D_k C_k^{t+1} + F_k$$  \hspace{1cm} (5)

with $0 \leq \Delta^t_{l,m} \leq 1$

Eq.(5) can be recast with terms containing species concentrations at time $t + 1$ on the left-hand side and the others on the right-hand side:

$$C_k^{t+1} - \sum_{l,m} \sigma K_{l,m} \delta t [\Delta^t_{l,m} C_l^{t+1} C_m^{t+1} + (1 - \Delta^t_{l,m}) C_l^{t+1} C_m^t] + D_k \delta t C_k^{t+1} = C_k^t + F_k \delta t$$  \hspace{1cm} (6)

that can be reformulated in a matrix form:

$$(I - M \delta t) C^{t+1} = C^t + F \delta t$$  \hspace{1cm} (7)

5
with the matrix $M$, an approximation of the Jacobian $J$, containing species concentrations at time $t$ and values of $\Delta_{l,m}$ evaluated also at time $t$.

Compared to other one step semi-implicit schemes like SIS (i.e. Ramarosson et al. 1994), one specificity of our scheme lies in the evaluation of $\Delta_{l,m}^t$. Let us consider the system of a single reaction between species $C_l$ and $C_m$ with a reaction rate constant $K_{l,m}$. If the initial values of the concentrations are equal, $C_l^0 = C_m^0 = C^0$, the exact solution of the system gives a hyperbolic decay for the concentrations:

$$C_l(t) = C_m(t) = C^0/(1 + K_{l,m}C^0t)$$

(8)

This solution is obtained exactly using the discretization given by Eq. (6) with $\Delta_{l,m} = 1/2$. If $C_l^0 \gg C_m^0$, the evolution of the lowest concentration $C_m$ shows a quasi exponential decay with an e-folding time $\tau = 1/(K_{l,m}C_l^0)$ while the concentration $C_l$ reaches its steady state value $C_l^0 - C_m^0$ that does not depart strongly from its initial value. In that case, in order to maximize the timestep and to increase the stability of the scheme, there is advantage in treating the evolution of the shorter lived species $C_m$ as implicitly as possible by giving more weight to the term $C_l^0C_m^t$ in Eq. (6). This is obtained if $\Delta_{l,m}$ tends to 1. Those simple considerations lead us to introduce the following function for $\Delta_{l,m}^t$ that depends on the concentrations at time $t$:

$$\Delta_{l,m}^t = (C_l^t)^\beta/((C_l^t)^\beta + (C_m^t)^\beta)$$

(9)

with $\beta \geq 1$. With this formulation the value of $\Delta_{l,m}$ has the required properties: $\Delta_{l,m} = 1/2$ if $C_l = C_m$ and $\Delta_{l,m} \to 1$ if $C_l \gg C_m$. The value of $\beta$ controls the sensitivity of $\Delta_{l,m}^t$ as a function of the concentrations. Large values of $\beta$ favor the implicit treatment for the lowest concentrations. Positive values of $\beta$ lower than 1 could also be used but they may not discriminate enough the treatment of species according to their concentrations. For the situations studied in this paper the numerical simulations did not show a large sensitivity to this parameter, which was fixed to 1 hereafter.

Furthermore, the use of Eq. (9) to calculate $\Delta_{l,m}^t$ and evaluate $M$, the approximate Jacobian matrix, gives interesting properties to our scheme:

- The oscillations from odd to even timesteps that can appear in the numerical solution of Eq. (6) when the semi-implicit scheme is centered and symmetrical (i.e. Shure and Rosset, 1994), as would be if the fixed value $\Delta_{l,m}^t = 1/2$ was adopted, is damped with the evaluation of $\Delta_{l,m}^t$ by Eq (9).

- Since the largest terms contributing to the evolution of the shortest lived species are treated implicitly the system increases in stability. Larger timesteps can be used and positive values for the concentrations are more easily preserved.

- All the species are treated in the same manner without any a priori considerations on lifetimes or abundances. For instance in the case of the Earth composition $O_2$ is treated like the other species even if its chemical sources and sinks are negligible. Since the concentration of $O_2$ is much larger than the other species concentrations, any species reacting with $O_2$ will be treated implicitly. This is the case for example of atomic oxygen $O$ reacting with $O_2$ to form $O_3$. The corresponding term in Eq. (6) for the $O$ tendency will be $\Delta O_2^tO_3^{t+1} + (1 - \Delta)O_2^{t+1}O_3^t$ which reduces to $O_2^tO_3^{t+1}$ since $\Delta = (O_2^t)^3/((O_2^t)^3 + (O_3^t)^3) \approx 1$. The option to treat all the species in the same manner simplifies the programming of
the scheme and allows the solver to be easily adapted to various chemical systems. An example is given in section 5 with
the simulation of the atmospheric composition of the planet Mars.

Once the matrix $M$ is evaluated and the timestep is determined (see the next section), the solver computes the solution to
the system of linearized equations (7), which becomes a possible computational bottleneck. Our approach is to use standard
methods and well optimized software libraries.

Our baseline option is to use the direct solver DGESV of the Lapack library that solves system (6) by LU decomposition.
Therefore no extra specific routine associated with the chemical mechanism is needed and the optimization on the computer
used is left to the implementation of the Lapack library. As reported below this option works well and gives accurate results
even for comprehensive mechanisms involving hundreds of species or more.

To reduce the computational cost other options for the resolution of the linear system have been investigated. Two
iterative solvers have been tested. The first one is an implementation of the Gauss-Seidel algorithm. This algorithm has been
used with success to solve stiff systems from chemical kinetics (Verwer et al., 1994; Menut et al., 2013). For the cases studied
in the following sections the Gauss-Seidel algorithm was found to be efficient with a good rate of convergence in most cases.
Although in specific situations where the system is largely driven out of equilibrium, for instance during day-night transitions
and for large surface emissions, the number of iterations could increase by one order of magnitude to obtain the required
accuracy.

A second iterative algorithm has been implemented, the generalized minimal residual method (GMRES). The method ap-
proximates the solution by a vector in a Krylov subspace with minimal residual norm. The Arnoldi iteration algorithm is used
to find this vector. The GMRES method was developed by Saad and Schultz (1986) and further described by Saad et al. (2003).
In order to accelerate the convergence, preconditioning techniques are used. An efficient one was obtained by introducing the
matrix $B$ using the lower triangular part of the $A = I - M \delta t$ matrix to compute an approximation of $A^{-1}$ and apply GM-
RES to the solution of the right-preconditioned linear system $ABC^* = C^t + F \delta t$ where $C^{t+1} = BC^*$. For the implementation
discussed hereafter the GMRES method needs less iterations than the Gauss-Seidel one, especially in situations where the
Gauss-Seidel algorithm shows slower convergence, and was found to speed up the computation by at least a factor 2 compared
to the DGESV implementation.

2.3 Time stepping

Since the time discretization adopted to solve system (7) is first order accurate, the choice of the timestep $\delta t$ is important to
obtain a solution with a desired accuracy. In our applications the evolution of the species over rather large time intervals $\Delta t$ is
required. $\Delta t$ is determined by other physical processes than chemistry, for instance advection, convection or vertical diffusion,
and is often too large to be used directly to solve Eq. (7) without encountering numerical instabilities and loss of accuracy.
For example in the 3D model results discussed in section 4, the time interval $\Delta t = 15$ minutes is determined by horizontal
advection whereas the chemical timestep has to be decreased to a few seconds in situations where the chemical state is driven
far from a quasi steady state.
Therefore a variable stepsize strategy has to be implemented with the time interval $\Delta t$ divided in $n$ successive integrations of the chemical system with timesteps $\delta t_n$.

The choice of $\delta t_n$ is done iteratively using a strategy similar to the one described by Verwer (1994). First a local error indicator $E$ is computed:

$$E^{k+1} = \max_m \left( \frac{2}{(\gamma + 1)} \left( \gamma C_m^{k+1} - (1 + \gamma)C_m^n + C_m^{n-1} \right) / W_m \right)$$

with

$$W_m = ATOL + RTOL C_m^n$$

where

$$\gamma = \frac{\delta t_{k+1}}{\delta t_n}, \quad \delta t_{k+1} \text{ is a first guess timestep, } C_m^{k+1} \text{ the concentration of the species } m \text{ at the iteration } k + 1, \quad ATOL \text{ and } RTOL \text{ are absolute and relative error tolerance. } C_m^{k+1} \text{ is evaluated using Eq. (2) with } C_m^n \text{ as initial concentration and the timestep } \delta t_{k+1}.$$  

$E^{k+1}$ depends on the curvature of the solution, a measure of the departure of the solution from linearity. If $E^{k+1} \leq 1$ the timestep $\delta t_{k+1}$ is adopted ($\delta t_{n+1} = \delta t_{k+1}$) otherwise a new timestep is estimated by:

$$\delta t_{k+2} = \max(0.1, \min(2.0, 0.8/\sqrt{E^{k+1}})) \delta t_{k+1}$$

Then a new value $C_m^{k+2}$ is evaluated followed by the computation of $E^{k+2}$, and so on until convergence. In practice the convergence is obtained within a few iterations, less than 5 in the cases reported thereafter. Those iterations have a low computational cost because the resolution solution of Eq.(2) at each iteration involves only diagonal matrices. Once the value of $\delta t_{n+1}$ is determined the concentration $C_m^{n+1}$ is obtained by resolution-the solution of Eq.(7).

For the first iteration species concentrations at two consecutive times and a first guess timestep are needed. To avoid storing concentrations at consecutive times we assume that at the beginning of the iterative process the system is in a steady state, $C_m^n = C_m^{n-1}$ in Eq. (10), and the first guess timestep is set to its largest possible value $\Delta t$. To secure the iterative process a minimum timestep, $\delta t_{\text{min}}$, is also prescribed in order to limit the number of iterations. The value of this minimum timestep is left to the user who has to choose a value consistent with the error tolerance parameters.

3 Tests and validation

To validate and evaluate the performances of ASIS and the associated numerical codes several case studies have been used. All these cases reported in this section are based on the RACMOBUS chemical scheme used within the MOCAGE CTM. RACMOBUS is a combination of the REPROBUS scheme adapted to the stratosphere and the free troposphere (Lefèvre et al., 1994), and the RACM scheme (Stockwell et al., 1997) that treats the urban polluted earth atmosphere with addition of volatile organic compounds, VOCs, and their degradation products. Table 1 lists the chemical species taken into account, the overall scheme includes about 120 species linked by 200 gas-phase reactions and photodissociations. The photodissociation rates are calculated every 15 minutes using the Tropospheric Ultraviolet and Visible (TUV) radiation model version 5.2 (Madronich and Flocke, 1998) for conditions corresponding to the equinox at 30° latitude.
<table>
<thead>
<tr>
<th>Table 1. List of species used for the box-model simulations. The upper part of the table lists the species active in the free troposphere and the stratosphere. The lower part lists additional VOC species or generic species involved in the RACM mechanism (Stockwell et al., 1997).</th>
</tr>
</thead>
<tbody>
<tr>
<td>O(^1D), O(^3P), O_2, O_3,</td>
</tr>
<tr>
<td>N, N_2O, NO, NO_2, NO_3, N_2O_5, HNO_2, HNO_3, HNO_3(gas&amp;solid),</td>
</tr>
<tr>
<td>CH_4, CH_2O, CH_3, CH_3O, CH_3O, CHO, CH_2O_2, CH_3O_2, CO, CO_2</td>
</tr>
<tr>
<td>H_2, H_2O(gas&amp;solid), H, OH, HO_2, H_2O_2,</td>
</tr>
<tr>
<td>SO_2, H_2SO_4, DMS, SULFATE</td>
</tr>
<tr>
<td>CCl_4, CFC−(11&amp;12&amp;113&amp;114&amp;115), HCFC−22,</td>
</tr>
<tr>
<td>HA−(1202&amp;1211&amp;1301), CH_3Cl, CHCl_3, CH_2CCl_3,</td>
</tr>
<tr>
<td>Cl, Cl_2, ClO, OCIO, ClO_2, Cl_2O_2, HOCl, HCl, ClONO_2</td>
</tr>
<tr>
<td>CH_3Br, CHBr_3,</td>
</tr>
<tr>
<td>Br, Br_2, BrO, HBr, HOBr, BrONO_2, BrCl</td>
</tr>
<tr>
<td>ACO_3, ADDC, ADDT, ADDX, ALD, API, APIP,</td>
</tr>
<tr>
<td>CLS, CSLP, DCB, DIEN, ETE, ETEP, ETH, ETHP,</td>
</tr>
<tr>
<td>GLY, HC_3, HC_3P, HC_5, HC_5P, HC_8, HC_8P, HKET, ISO, ISOP</td>
</tr>
<tr>
<td>KET, KETP, LIM, LIMP, MACR, MGLY, MO_2</td>
</tr>
<tr>
<td>OLI, OLIP, OLND, OLNN, OLT, OLTP, ONIT, OP1, OP2</td>
</tr>
<tr>
<td>PAA, PAN, PHO, TC_3O_3, TOL, TOLP, TPAN,</td>
</tr>
<tr>
<td>UDD, XO_2, XYL, XYLP</td>
</tr>
</tbody>
</table>

Two test cases are used to evaluate the accuracy and performance of the ASIS scheme. The first one is based on the FLUX test case described by Crassier et al. (2000). It corresponds to a ground level situation in an urban polluted area. The list of species and fluxes emitted at the surface is given in table 2. The emissions are injected in a boundary layer with a 2000 m constant thickness weighted by an emission factor of 0.6. This leads to a constant tendency $F$ in Eq. (4) for the emitted species. The initial concentrations are given in table 3, the atmospheric temperature is set to 298 K and the ground pressure is 1000 hPa.

The second case, STRATO, is representative of situations encountered in the middle stratosphere. The initial concentrations for this case are given in table 3. The atmospheric temperature is 215 K and the pressure is 50 hPa. For both cases the integration starts at midnight, stops 24 h after, and the photodissociation rates are updated every 15 minutes.

3.1 The FLUX case

To assess the performances of ASIS two reference simulations have been obtained for the FLUX case using Rosenbrock’s and Gear’s BDF solvers (referred hereafter as R1 and G1). Those solvers use respectively the ode23s and ode15s codes from the Matlab ODE suite (Shampine and Reichelt, 1997, Ashino et al., 2000). For the Rosenbrock’s scheme a 3 stage algorithm is used and the simulations are third order accurate. For the Gear’s scheme the third order accurate option was also chosen. The
Table 2. VOC emissions in the FLUX test case

<table>
<thead>
<tr>
<th>Species</th>
<th>Emission ((10^{10} \text{ molecules cm}^{-2} \text{s}^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO</td>
<td>121.29</td>
</tr>
<tr>
<td>CO</td>
<td>2500</td>
</tr>
<tr>
<td>CH₄</td>
<td>802</td>
</tr>
<tr>
<td>ETH</td>
<td>6.25</td>
</tr>
<tr>
<td>HC₃</td>
<td>37.67</td>
</tr>
<tr>
<td>HC₅</td>
<td>44.43</td>
</tr>
<tr>
<td>HC₈</td>
<td>19.14</td>
</tr>
<tr>
<td>ETE</td>
<td>22.33</td>
</tr>
<tr>
<td>OLT</td>
<td>39.67</td>
</tr>
<tr>
<td>OL1</td>
<td>6.37</td>
</tr>
<tr>
<td>TOL</td>
<td>9.02</td>
</tr>
<tr>
<td>CH₂O</td>
<td>5.77</td>
</tr>
<tr>
<td>ALD</td>
<td>14.45</td>
</tr>
<tr>
<td>KET</td>
<td>5.70</td>
</tr>
<tr>
<td>XYL</td>
<td>14.55</td>
</tr>
<tr>
<td>CSL</td>
<td>3.68</td>
</tr>
</tbody>
</table>

Table 3. Initial conditions for the FLUX and STRATO test cases

<table>
<thead>
<tr>
<th>Species</th>
<th>STRATO (\text{vmr})</th>
<th>FLUX (\text{vmr})</th>
</tr>
</thead>
<tbody>
<tr>
<td>O₃</td>
<td>1.0 (10^{-9})</td>
<td>50 (10^{-9})</td>
</tr>
<tr>
<td>CO₂</td>
<td>330 (10^{-9})</td>
<td>330 (10^{-9})</td>
</tr>
<tr>
<td>N₂O</td>
<td>300 (10^{-9})</td>
<td>310 (10^{-9})</td>
</tr>
<tr>
<td>NO</td>
<td>1.0 (10^{-9})</td>
<td>2.0 (10^{-9})</td>
</tr>
<tr>
<td>NO₂</td>
<td>0.3 (10^{-6})</td>
<td>1.0 (10^{-9})</td>
</tr>
<tr>
<td>HNO₃</td>
<td>4.0 (10^{-9})</td>
<td>0.5 (10^{-9})</td>
</tr>
<tr>
<td>CH₄</td>
<td>1.4 (10^{-6})</td>
<td>1.6 (10^{-6})</td>
</tr>
<tr>
<td>CO</td>
<td>20 (10^{-9})</td>
<td>150 (10^{-9})</td>
</tr>
<tr>
<td>HCl</td>
<td>2.5 (10^{-9})</td>
<td>1.0 (10^{-12})</td>
</tr>
<tr>
<td>ClONO₂</td>
<td>0.3 (10^{-9})</td>
<td>--</td>
</tr>
<tr>
<td>BrO</td>
<td>15 (10^{-12})</td>
<td>1.0 (10^{-13})</td>
</tr>
</tbody>
</table>

In the most accurate simulations R1 and G1 (see table 4) the relative tolerance RTOL was set to 0.001 and the absolute
tolerance ATOL equals $10^4$ molecules cm$^{-3}$ for all species. With the Rosenbock’s solver additional simulations with higher tolerance values have been performed, R2 with RTOL=0.01 and R3 with RTOL=0.025.

The same FLUX case is integrated using the ASIS solver. In this simulation, a first simulation noted A1, ASIS uses a RTOL value of 0.001 and a minimum timestep of 1s. For the resolution solution of the linear system associated with ASIS, the DGESV code of the Lapack library is used. A To compare with the Rosenbrock’s solver a second simulation A2 has been obtained with the same settings as A1 but with a higher relative tolerance value of 0.01, and a third one A3 with a tolerance value of 0.025. For all experiments the FLUX case is integrated over 24 h. The settings used in the overall simulations are given in Table 4.

Figures 1 and 2 show the evolution of some key species for each experiment and the relative differences from the R1 experiment. Those results are representative of all the species. As expected the R1, G1 and A1 simulations give very close results. R1 and G1 show relative differences below 0.1 % consistent with the value chosen for RTOL. A1 results are comparable with differences in the 0.1-0.2 % range, except at the beginning of the simulation when the chemical state is out of equilibrium and during day-night transitions. In those situations the differences between A1 and R1 or G1 can reach 0.5 %. As expected from the choice of a higher value for RTOL, the A2 experiment shows less accuracy but is still in the range of 0.5% compared to the other experiments. The A3 experiment have has differences below 2% with the other experiments. For most of the atmospheric simulations an accuracy below 1% is sufficient for the longest lived species, and even larger values are acceptable for short lived species if they are transient, given the uncertainties in the representation of the other processes and the inaccuracies introduced by their resolution solution by a series of successive operators.

The efficiency of ASIS can be first evaluated by comparison of the mean timesteps (table 4). For simulations R1 and G1 the mean timesteps are between 25 and 40 s. Since ASIS uses a first order scheme to maintain good accuracy the mean timestep is lowered, in the 5 s range for the A1 experiment. However ASIS is a one stage scheme (only one linear system is solved by timestep) compared to R1 and G1 that need 3 or more stages. The amount of computation is therefore comparable. When the relative tolerance is increased the mean timestep of ASIS increases. For the A2 experiment it is 25 s, identical to R1, and up to 49s for A3. Since for most of atmospheric simulations a relative tolerance of 0.01 to 0.025 seems to be sufficient the ASIS solver gives acceptable solutions with less computation than the higher order schemes.

The efficiency of ASIS in terms of CPU time has been evaluated within the Matlab environment. Table 4 gives the ratio of CPU time used for each simulation relative to the R1 case. The ode23s code used to run the R cases needs the implementation

<table>
<thead>
<tr>
<th>Method/code</th>
<th>R1</th>
<th>R2</th>
<th>R3</th>
<th>G1</th>
<th>A1</th>
<th>A2</th>
<th>A3</th>
</tr>
</thead>
<tbody>
<tr>
<td>RTOL</td>
<td>0.001</td>
<td>0.01</td>
<td>0.025</td>
<td>0.001</td>
<td>0.001</td>
<td>0.01</td>
<td>0.025</td>
</tr>
<tr>
<td>δt (\text{m} )</td>
<td>39s</td>
<td>44s</td>
<td>46s</td>
<td>25s</td>
<td>4.7s</td>
<td>25s</td>
<td>49s</td>
</tr>
<tr>
<td>CPU-Ratio</td>
<td>1</td>
<td>0.94</td>
<td>0.92</td>
<td>0.82</td>
<td>3.8</td>
<td>0.97</td>
<td>0.72</td>
</tr>
</tbody>
</table>

Table 4. Mean timesteps: List of the different settings used by the 0D model for the FLUX test case. \(\delta t_m\) is the mean time step and CPU-Ratio is the CPU time used in each simulation relative to R1. The simulations are performed in the Matlab environment.
of two subroutines, one that computes the species tendencies and one that gives the Jacobian of the system. If the latter is not provided the ode23s code computes an approximation of the Jacobian by differentiation and the CPU cost increases by a factor 2 to 10. As can be seen from table 4 the CPU cost of ASIS is comparable or lower than the ode23s cost for relative tolerance values larger than 0.01.

An important point to mention is that within the Matlab environment the CPU cost does not come from the linear algebra parts of the algorithms but from the evaluation of tendencies and Jacobian matrices. Therefore it is very dependant upon the chemical system and the details of the programing of the associated subroutines. The situation is quite different within the Fortran environment. With the Fortran version of ASIS the CPU cost for the calculation of the approximated Jacobian (the matrix M of Eq. 7) is negligible compared to the linear algebra computations. This is because the compiler handles efficiently the associated subroutine (fill_matrix, see section 7) that contains frequent indirect addressing. It is not possible to evaluate if this is also the case with all the codes based on Rosenbrock’s algorithm, but if it is so ASIS should perform well when the mean time steps are comparable since it needs less linear algebra computations.

For the A1 and A2 - A experiments ASIS uses the DGESV code for the resolution solution of the linear systems. To save computational time two iterative solvers have been tested, one using the Gauss-Seidel algorithm, the other the GMRES method. Both solvers used the same criterion for convergence (tolerance for convergence set to 10\(^{-14}\)). For the GMRES method the preconditioning technique described in section 2.1 is implemented. With those settings the experiment A2 has been repeated.

The results are practically identical to the solution obtained using the DGESV code. Figure 2 shows for example differences, the differences between the solutions are below 0.02 % for the simulation of all the species concentrations. The simulation with the Gauss-Seidel algorithm shows good efficiency in terms of mean number of iterations, but requires 6 to 10 times more iterations when the system is driven out of equilibrium during day-night transitions. In the present simulations, using Using GMRES was found more stable and efficient with less than 10 iterations needed to solve the linear systems and twice less computational time (using the Fortran version of the code) compared to the simulation using DGESV.

From the simulations of this FLUX case, which is rather representative of situations encountered in polluted earth boundary layers, it can be concluded that the ASIS solver performs well compared to higher order schemes when moderate accuracy is required. Apart from tolerance parameters and the choice of a minimum timestep no specific tuning is required. The one step implicit scheme gains in efficiency when coupled to the GMRES iterative solver used for the resolution solution of the linear systems.

FLUX case. Time evolution of for the A2 experiment. Left panel: evolution of the concentration. Right panel: relative differences of the solutions using the iterative Gauss-Seidel (green) and GMRES (blue) algorithms compared to the direct method DGESV to solve the linear systems associated to the ASIS solver.

3.2 The STRATO case

The STRATO case differs from the FLUX case in the dominant chemical regimes involved. In the FLUX case the VOC decomposition during day and night dominates the system. With the STRATO case the chemistry is dominated by NOx, HOx,
Figure 1. FLUX case. Time evolution of selected species ($O_3$, $NO_2$, $NO_3$, $OH$) for the R1, G1, A1, A2, and A3 experiments. The left column shows the volume mixing ratios and the right one the differences in % relative to the R1 experiment. The color code is the following: blue for G1, orange for A1, red for A2, and purple for A3.
Figure 2. FLUX case. Same as figure 1 for CH$_2$O, HC8P (peroxy radicals) and PAN (peroxyacetyl nitrate).
Clx catalytic cycles and the ozone content. The stiffness of the system is less stringent and rapid variations in the concentrations of the species are tightly linked to the variations of the insulation at sunrise and sunset.

For this case two simulations have been performed. The first one, $R2$, uses the Rosenbrock’s algorithm with settings similar to experiment R1. For the second one, $A4AS2$, the ASIS solver is used with settings similar to experiment A2 and with the iterative linear solver GMRES. The two simulations show results consistent with the findings for the FLUX case. The mean timestep are very similar for both experiments, 49 s for $R2$ and 41.4 s for $A4AS2$. As expected the timestep decreases in ASIS at sunrise and sunset when the stiffness of the system is at maximum. Figure 4-3 shows the number of timesteps for every 15 minute interval for the 24 hour simulation of experiment $A4AS2$. Apart from the very beginning of the simulation that starts in a situation out of equilibrium, the largest values are found at sunrise and sunset in the 200 range. It corresponds to timesteps of about 4.5 s.

In terms of accuracy, the $A4AS2$ experiment gives results that depart less than 1% compared to $R2RS1$. This is consistent with the chosen value of 0.01 for RTOL. Figure 5-4 shows that the lowest accuracy is found at sunrise and sunset when the short lived radical species have the largest variations. Those transition situations are the most difficult because not only the accuracy must be maintained but spurious numerical oscillations must be avoided. ASIS performs well here and adapts its timestep automatically to reach the required accuracy. The numerical treatment adopted to calculate an approximation of the
Jacobian (Eq. 9 with $\beta = 1$) contributes greatly to damp-reduce numerical oscillations without significant degradation of the accuracy of the solution.

Equally, the approximations in the Jacobian are efficient to prevent the development of negative mixing ratios. In the two cases FLUX and STRATO, we did not encounter any significant (larger than $ATOL$) negative values during the course of the simulation and all the concentrations remain positive at the end of the 15 minute intervals before the photodissociation rates are updated.

In summary, the results of the two test cases confirm the properties searched-targeted in the design of ASIS. At the moderate accuracy required for atmospheric simulations the ASIS solver compares well with higher order schemes, and limits the computational cost while assuring mass conservation. The next sections illustrate how it performs in more realistic situations with implementations in state of the art global chemical transport models for Earth and Mars atmospheres.

4 Implementation within the MOCAGE model

For this study we have used the global version of the chemical transport model MOCAGE with an horizontal resolution of $2^\circ \times 2^\circ$ and 47 levels in the vertical from ground to 5 hPa. The chemical scheme is RACMOBUS, identical to the one used for the test cases of section 3. In addition to chemistry and transport by the large scale winds and by convection, the model includes the main processes that contribute to the sources and sinks of the species: surface emissions, scavenging by rain, dry and wet depositions. The timesteps for these processes is 15 minutes, photodissociation and chemical rate constants are updated at the same frequency. We report here simulations over three months from the beginning of August to the end of October 2011. Wind and temperature fields come from the operational weather analyses of the ECMWF. They are updated every 3 hours and linearly interpolated in between these time intervals.

The reference simulation, MR, uses the original solver for chemistry, an iterative semi-implicit scheme with assumptions of equilibrium for short lived species and species lumping for $NO_x$ and $Cl_x$ families. The chemical timestep varies with altitude but is kept constant during the model integration. It increases from 20 s in the planetary boundary layer to 15 minutes in the stratosphere.

The simulation with the ASIS solver, MA, uses the same configuration for MOCAGE as MR except that the original chemical solver is replaced by ASIS with settings similar to experiment A3: $RTOL = 0.025$, $ATOL = 10^{4}$ molecules cm$^{-3}$, a minimum timestep of 5s, and the GMRES solver for the resolution-solution of the linear systems.

The characteristics of the ASIS functioning implemented within MOCAGE can be first examined by the diagnostic of the number of sub-timesteps for chemistry. Figure 6-5 shows this number for 3 different levels for a date corresponding to the 15th of September at mid-day. In the mid-stratosphere, at 50 hPa, the number of sub-timesteps varies in accordance with what was found for the STRATO test case. At mid day or night the chemical system is in quasi steady state and this number is small, below 3. Close to the terminators this number increases up to 40-60 highlighting the change of regime of the chemical system when the photodissociation is activated or deactivated. During these transition phases the stiffness of the system increases and the sub-timesteps decrease to maintain the required accuracy. Also barely noticeable is an increase of the number of sub-
Figure 4. STRATO case. Time evolution of selected species (CH$_2$O, NO$_2$, NO$_3$, OH) for the R2 RS1, and A4 AS2 experiments. The left column shows the mixing ratios or concentrations and the right one the differences in % for AS2 relative to the R2 RS1 experiment.
timesteps over the Antarctica coast at the edge of the polar vortex. In these regions the heterogeneous reactions acting at the surface of polar clouds are activated introducing disequilibrium of driving the concentrations of the chlorine species out of equilibrium. It leads to a reduction of the sub-timesteps to cope with the rapid variations of the chemical composition of the air masses.

In the middle troposphere the same behavior is encountered near the terminators with a tendency to maintain reduced sub-timesteps during longer periods after sunrise or before sunset (figure 6). An increase of the number of sub-timesteps is also encountered over the African continent at low latitudes. Those regions are prone to convective activity and injection of species by convection is activated leaving air masses far from chemical steady-state. Since the chemical evolution of the species is calculated after the transport processes, ASIS starts with a situation far from a chemical equilibrium and the number of sub-timesteps increases.

At the surface, figure 6 shows the same characteristics as in the mid-troposphere with an increase of the number of sub-timesteps at the terminators and over the continents. Over the continents the surface emissions play a larger role than convection to destabilize the chemical system. Within MOCAGE the emissions are calculated according to inventories and deposited in the boundary layer. This is treated as an isolated process that changes the concentrations. As a result ASIS starts with situations out of chemical equilibrium and adopts small sub-timesteps, about 20 s compared to 60 s over the oceans.

Except for noticeable cases that are discussed hereafter, the species distributions of the MA simulation are close to those obtained in MR. As an illustration figure 2 shows the zonally averaged distributions of $O_3$, CO, OH and HNO$_3$ for the month of September. In most altitudes the differences are below 10% with the largest differences in SH high latitudes in the lower stratosphere. Similar differences are found for the other species except for the NO$_x$ species in the lower troposphere and the chlorine species in the high latitudes of the SH during the formation of the stratospheric ozone hole.

In the lower troposphere, examination of the code of the MR simulation reveals that approximations and steady-state assumptions are made for the computation of the night-time NO$_2$/NO$_3$/N$_2$O$_5$ system. These approximations are valid in the stratosphere but fail in the lower troposphere where the pressure and temperature are larger. As a result the MR simulation under-evaluates the concentrations of NO$_3$ and N$_2$O$_5$.

Figure 9 shows for example the distributions of NO$_2$, HNO$_3$ and N$_2$O$_5$ at the lower level near the surface averaged over the month of October. In the region of surface emissions the MR simulation strongly underestimates the N$_2$O$_5$ concentrations. Since the chemical scheme adopted for the present simulations does not include the formation of HNO$_3$ by the hydrolysis reaction of N$_2$O$_5$ on aerosols surface (Dentener and Crutzen, 1993), it has not a major influence on the other species. Nevertheless, the maximum values for HNO$_3$ and NO$_2$ are larger in the MA simulation than in the MR simulation.

Another significant difference between MR and MA is found in the simulation of the ClO$_x$ system in the lower stratosphere at high SH latitudes. In late August and early September the solar radiation comes back at high latitudes and the lower stratospheric O$_3$ is destroyed by catalytic cycles involving chlorine radicals (Solomon, 1999). The chlorine radical concentrations are enhanced by the heterogeneous reactions on PSC’s surface that convert HCl and ClONO$_2$ into Cl$_2$ that is photodissociated to form the chlorine radicals. In addition, the catalytic destruction of O$_3$ involves also the bromine species.
Figure 5. Number of sub-timesteps per timestep of 15 minutes in the MA simulation for the 15th of September mid-day. 3 levels are presented representative of the stratosphere (50 hPa), the mid-troposphere (540 hPa) and the surface.
Figure 6. Zonal mean distributions of O$_3$, CO, OH and HNO$_3$ for the month of September. The left columns shows results for the reference simulation, MR, the right column shows results of the MA simulation with the use of the ASIS solver.

In the air masses prone to heterogeneous reactions on PSC the composition changes rapidly at sunrise and non-linear processes, like the formation of Cl$_2$O$_2$, a key species for the O$_3$ destruction, play a major role. As a result the chemical system is very stiff and the ASIS solver diminishes the chemical timestep to a few seconds to maintain good accuracy. In these transient situations the original code in MR does not change its settings and a fixed timestep of 15 minutes is used. It results in that the MR simulation produces a much more pronounced ozone depletion over Antarctica than the MA simulation. MR calculates ozone column contents as low as 100 Dobson Units (DU) whereas the MA simulation maintains values in the range of 150 DU. This is well illustrated in figure 8-9 that shows the evolution of the total ozone columns over two Antarctic stations, Dumont d’Urville and Dôme C. For these 2 stations the measurements done by SAOZ instruments (Pommereau et al., 1988) at sunrise and sunset are also presented (data available at http://saoz.obs.uvSQ.fr).
Figure 7. Monthly mean distributions of NO$_2$, HNO$_3$ and N$_2$O$_5$ at the surface for the month of October after a two month integration. The left column shows results of the reference simulation, MR, the right column shows results of the MA simulation with the use of the ASIS solver. The MR simulation under-evaluates the N$_2$O$_5$ in the lower troposphere.

Starting around 220 julian day the MR and MA simulations start to diverge. Over Dumont d’Urville, the station that sees first the return of the sunlight, the ozone decrease is about 50 % larger in the MR simulation than for MA. By day 260 the ozone column is just above 150 DU whereas it is in the 200 DU range in the MA simulation. Clearly the MA simulation is in better agreement with the SAOZ measurements.

The same behavior is seen for the Dôme C station. The ozone depletion starts slightly later, around day 240. In the MR simulation the depletion is very pronounced and the ozone column diminishes rapidly in a few days from 240 to 150 DU, and further decreases at a slower rate to reach a minimum of 100 DU at day 260. The MA simulation shows a more continuous decrease from day 240 to 260 with an ozone column reaching a minimum of 150 DU. The MA simulation is here again in very good agreement with the SAOZ observations.
Implementation of the ASIS solver within MOCAGE has thus revealed two weaknesses of the original model. One problem is in a limitation on the validity of assumptions made to compute the night-time distribution of the NOx species. It can be solved by adequate coding. The other one is a lack of accuracy in the resolution of the chemical system in specific situations in the lower stratosphere. This can certainly be avoided by a drastic reduction of the timestep, but it would need the implementation of a time varying timestep strategy somewhat similar to the one adopted for ASIS.

Clearly the implementation of ASIS within MOCAGE is very beneficial to the model simulations and increases the confidence on the model results. In addition, further evolution of the model with adoption of different chemical schemes or addition of new reactions is very easy with ASIS.

There is however a price to pay in terms of computer time. Overall the MA simulation takes 4.7 times more computational time than the MR simulation. This number could be certainly decreased by further tuning of the parameters of the solver, RTOL, ATOL and δt_{min}, and maybe also by the use of the Gauss-Seidel algorithm instead of GMRES in situations where the solution of the linear system converges easily.

Our experience with ASIS shows that since various processes are computed by a series of operators the solver starts new timesteps with situations often out of chemical equilibrium and must use small sub-timesteps. To alleviate this, one possibility is that tendencies from these operators are computed and stored rather than used to update the species concentrations. The tendencies can then be used to solve the system though their introduction in the term $F$ of Eq. (7). We have tested this option for the species emissions at the surface and found that the number of sub-timesteps is decreased by a factor 2 in the lower troposphere. It remains to be seen if other processes can be treated that way. Emissions are the most straightforward because the resulting tendencies are positive and cannot lead to the calculation of negative concentrations.
Another issue lies in the parallelisation of the computations. In the reference simulation the computational cost is equal for each grid-point at a given level and good parallelisation is obtained with an equally spaced latitudinal band decomposition (and use of openMP directives). When ASIS is used the computational cost in each grid-point depends on the state of the chemical system. As illustrated in figure 6, in the stratosphere and upper troposphere more computer time is needed near the terminators and in case of PSCs induced chemistry. In the lower troposphere more computer time is spent in grid-points influenced by surface emissions, and convective and boundary layer transport processes. A speedup of 15 was however obtained for the MA simulation on our cluster computer (using one node and 16 cores of our BULL computer) with a decomposition that groups more longitudes in the SH than in the NH near the poles. But further tuning would be required if more nodes are to be used. This tuning could vary with season and additional parallelisation could be introduced with domain decomposition on the vertical.

5 Implementation within the LMD Mars model

To illustrate the versatility of the ASIS solver, we present results of the implementation of ASIS in the LMD Mars model with photochemistry (Lefèvre et al., 2004). This Mars GCM describes the evolution of 19 species (table 5) by means of 54 chemical or photolytic reactions. The bulk atmosphere of Mars is composed of 95% of \( \text{CO}_2 \) with trace amounts of \( \text{H}_2\text{O} \). As a result, the only processes that initiate Martian photochemistry are the photolysis of \( \text{CO}_2 \) and \( \text{H}_2\text{O} \) by ultraviolet solar light. Therefore, the photochemistry of the lower atmosphere of Mars can be summarized by the interactions between the oxygenated species \( \text{O}(^1\text{D}), \text{O}, \text{O}_3 \) produced by \( \text{CO}_2 \) photolysis and the hydrogen radicals \( \text{H}, \text{OH}, \text{HO}_2 \) produced by \( \text{H}_2\text{O} \) photolysis. These processes are similar to those occurring in the Earth’s mesosphere, with comparable conditions of pressure and temperature.

In the standard version described in Lefèvre at al. (2004), the LMD GCM with photochemistry uses the Euler backward method (EB) expressed in (3) to solve its chemical system. As mentioned earlier, this method is positive, stable, and can be computationally effective but does not maintain mass conservation. Iterative evaluations of \( C^{t+1} \) are performed in the lower atmosphere of Mars to reduce this problem. In the Mars thermosphere, another option is used in the LMD model which consists in shortening the timestep \( \delta t \) according to the species with the shortest lifetime (González-Galindo et al., 2009). In both cases, species lumping and assumptions of photochemical equilibrium are used to increase accuracy and avoid very small timesteps. However, conditions of photochemical equilibrium change at night and are also very dependent on altitude. For instance, on Mars, the lifetimes of \( \text{O}(^3\text{P}) \) and \( \text{H} \) vary between less than 1 second near the surface to several years at 100 km. Such stark variation prevents assuming photochemical equilibrium or using Eq.(3) throughout the atmosphere. Thus, despite

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**Table 5.** List of species used in the Mars model simulations.

<table>
<thead>
<tr>
<th>Species</th>
</tr>
</thead>
<tbody>
<tr>
<td>O(^1\text{D})), O(^3\text{P})), O(_2), O(_3),</td>
</tr>
<tr>
<td>N, N(_2), NO, NO(_2), N(^2\text{D})),</td>
</tr>
<tr>
<td>H(<em>2), H(<em>2\text{O(gas&amp;solid)})), H(</em>\text{O}, H(</em>\text{O}_2), H(_2\text{O}_2),</td>
</tr>
<tr>
<td>CO, CO(_2), Ar</td>
</tr>
</tbody>
</table>

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its apparent simplicity, the Euler backward method may complicate the problem by requiring different treatments for specific species or specific parts of the atmosphere.

Figure 10-9 compares the results obtained with the Euler-Backward (EB) and ASIS solvers applied to a box-model version of the LMD Mars model. The atmospheric pressure/temperature is 5.4 hPa/212 K at the surface and 0.2 hPa/140 K at 30 km. In both cases the integration starts at noon, and stops after one Martian solar day of 24h40 mn. The photodissociation rates are calculated every 15 minutes using the TUV radiation model adapted to Mars. The timestep of the EB solver is fixed to $\delta t = 7.5$ minutes as done in the Mars GCM. ASIS uses the variable step size strategy described in section 2.3, bounded by a maximum value of 15 minutes and the minimum timestep of 10 s. RTOL is fixed to 0.05 and the ATOL density is equivalent to a corresponding volume mixing ratio of 10 ppt. ATOL is therefore variable with altitude. The resolution of the linear systems associated with ASIS is done using the DGESV direct solver. We found that these settings were adequate to reach a satisfying compromise between accuracy and computing time.

At the surface, figure 10-9 shows that the ASIS solver calculates an $O_3$ mixing ratio that is lower by 3 to 6 % compared to the EB solver. This difference is related to the lack of accuracy in the treatment of the HOx species in the EB solver, which assumes that OH and HO$_2$ are in photochemical equilibrium at all times within the HOx family. This assumption is close to reality during the day, but becomes problematic at sunrise and sunset and is wrong at night, when the HO$_2$ lifetime can reach several hours at the surface. As a result, the OH mixing ratio calculated by the EB solver is overestimated by a factor of 10 compared to ASIS, which does not require any a priori assumption on chemical lifetimes and provides an accurate solution throughout sunset and nighttime. At sunrise and sunset ASIS reduces the chemical timestep down to 10 s to solve the sharp transitions in the concentrations of short lived-species H, OH, O and NO. Outside these critical (but short) periods, the Martian settings of RTOL and ATOL allow timesteps that increase rapidly and may reach $\delta t = 15$ mn without sacrificing the accuracy.

Thus, in the example of figure 10-9, at the surface level, the number of chemical timesteps performed by ASIS over one Martian day is only 12 % larger than in the EB simulation.

The box-model simulations at 30 km are performed at the hygropause level where the production rate of HOx radicals by H$_2$O photolysis is the largest. This results in a maximum stiffness of the system at sunrise and sunset, when the H$_2$O photolysis rate varies rapidly. Those critical day/night transitions show large differences between the ASIS and the EB simulations. In the EB run, ozone is integrated implicitly by Eq.(3) at night and is assumed to be in photochemical equilibrium within the Ox family during the day. This abrupt change in treatment contrasts with the smooth transition carried out with the timestep adaptive scheme of ASIS. At the price of a strong reduction of the timestep to maintain the required accuracy, ASIS calculates an $O_3$ mixing ratio that is respectively 35 % larger and 20 % smaller than in the EB run at sunrise and sunset. Both solvers give the same results during the day. However, the more accurate description of the $O_3$ increase at sunset by ASIS induces a 5 % difference with the EB solver that persists into the night. Regarding OH, the simulation at 30 km confirms the weakness of the steady-state approximation for HOx at night in the EB scheme. In ASIS, the stiffness of the system diagnosed by the solver remains high in the first hours following sunset (due to strong curvature of the solution for H, not shown here) and leads to a reduction of the timestep to about 30s. The nighttime OH mixing ratio is larger by a factor 2 to 4 than in the
Figure 9. Comparison of the Euler-Backward (EB) and ASIS solvers applied to the Mars box-model version. The left column shows the mixing ratios of $O_3$ and OH and the right one the ratio between the ASIS and EB experiments. Results are presented at 30 km (top) and at the surface (bottom), for equatorial conditions in northern spring (solar longitude $L_s = 70^\circ$). Local noon is at day 0.5.
EB simulation. For this extreme case of stiffness in the Mars atmospheric chemistry, the total number of chemical timesteps executed by ASIS over one Martian day is 65% larger than in the EB simulation.

In its three-dimensional implementation, ASIS is called by the LMD GCM at each physical timestep $\Delta t = 15$ mn. The ASIS settings in the GCM are identical to those of the box-model presented earlier, i.e., the solver may select any sub-timestep value between $\Delta t$ and the minimum value $\delta t_{\text{min}} = 10$ s. To compare the GCM performances with ASIS and with the EB method, two simulations of 150 Martian solar days have been performed with each method starting with an identical initial situation.

Figure 11 shows the number of sub-timesteps per physical timestep of 15 mn in a GCM simulation of northern spring ($L_s = 70^\circ$) using ASIS. For the three levels presented here (surface, 30 km, 80 km) the number of sub-timesteps is equal to 1 or 2 for a large fraction of time. This is the case when the chemical system is in equilibrium, far from the terminators at night or during the day. As in the MOCAGE model, at the terminators the number of sub-timesteps increases dramatically to cope with the change of chemical regime at the day-night transitions. The maximum number (40-50) is found at sunrise at 30 km and is essentially driven by the abrupt changes in $\text{OH}$ and $\text{O_3}$ already seen in figure 10. At the surface, an increase in the number of sub-timesteps is also visible near the North pole. This is related to fast heterogeneous reactions of HOX species on water-ice clouds (Lefèvre et al., 2008), a process similar to that occurring with chlorine on Earth stratospheric clouds. In those cases ASIS adopts a smaller timestep to resolve with good accuracy a system that is locally away from chemical equilibrium.

Figure 12 compares at 30 km the results of GCM simulations using either the EB or the ASIS solver. Both schemes give distributions of $\text{O_3}$ and $\text{OH}$ that are in general very close during daytime and away from the terminators. At the terminators, ASIS calculates $\text{O_3}$ amounts that are about 50% larger than EB at sunrise and 25% smaller at sunset. These large differences are similar to those found with the box-model runs (figure 10.9) but are limited in time and space. However, the better description of $\text{O_3}$ by ASIS across the terminators may be crucial when comparing the GCM to Martian ozone measurements performed at the terminators by the solar occultation technique. Regarding $\text{OH}$, the GCM results confirm the poor description of the HOX chemistry by the EB scheme at the terminators and especially at night, with values 4 times. At night, $\text{OH}$ values calculated by EB are more than 30% smaller than with ASIS. The amount of nighttime $\text{OH}$ is small relative to daytime values. Thus, the bias in the EB scheme does not affect significantly the oxidizing capacity of Mars simulated by the GCM. Nevertheless, similarly to ozone, the more accurate description of $\text{OH}$ and the Martian nighttime chemistry in general is an important advantage brought by ASIS for the interpretation of the numerous observations of nightglow or measurements by stellar occultation carried out on that planet.

6 Conclusions

The ASIS solver has been designed to cope with the various situations encountered within the numerical simulation of the atmospheric chemistry. The main properties of the solver are mass conservation, an approximation of the Jacobian matrix of the chemical fluxes that stabilizes the associated system of differential equations, a time stepping varying module to control accuracy, and a code implementation that allows an easy adaptation to various chemical schemes. In box-model test
Figure 10. Number of sub-timesteps per time interval of 15 minutes in the LMD Mars GCM in northern spring (instantaneous result at solar longitude Ls = 70° and day 150 of the simulation). Three altitude levels are represented at 80 km (top), 30 km (middle), and the surface (bottom). Local noon is located at longitude zero. The white contour represents topography, with a 4-km interval.
Figure 11. Distribution of O₃ (left) and OH (right) at 30 km calculated by the LMD Mars GCM in northern spring (instantaneous result at solar longitude Ls = 70° and day 150 of the simulation). Top: Euler-Backward (EB) solver. Middle: ASIS solver. Bottom: relative difference (%) between ASIS and EB, using thresholds of 10 ppbv for O₃ and 10 pptv for OH. Local noon is located at longitude zero. The white contour represents topography, with a 4-km interval. Off-scale differences in O₃ and OH are limited to ± 50% and ± 30% respectively.
cases, the numerical solutions obtained with the ASIS solver were found in good agreement with those of multi-step algorithms like Rosenbrock’s and Gear’s methods.

The ASIS solver has been implemented in 3D models of the Earth (MOCAGE) and Mars (LMD model) planets. The results with MOCAGE using ASIS reveals two weaknesses of the original semi-implicit solver. One is related to the calculation of the partitioning of the NOx species at the surface and the other to an overestimation of the ozone depletion in the Antarctic stratospheric vortex in Spring. In the simulation of the Mars atmosphere ASIS gives more accurate simulations during day-night transitions and at night for the HOx species. These results stress the importance of having accurate enough numerical solutions, otherwise differences between model simulations and observations could be wrongly attributed to missing chemistry or misrepresentation of some physical processes.

The model simulations show the benefit of using a chemical solver with good properties such as mass conservation and controlled accuracy. This objective can be achieved using multi-step high order algorithms but the computational cost of those schemes increases rapidly with the number of species considered. Since ASIS is implicit and one step, a single linear system has to be solved for each iteration. For this, direct or iterative algorithms can be used. The direct methods based on LU decomposition see their computational cost increasing at least quadratically with the number of species, whereas the cost of iterative solvers increases rather linearly. Within ASIS we found that the GMRES iterative algorithm is stable and efficient, and is competitive in terms of CPU cost compared to the direct DGESV algorithm.

In atmospheric models the computational cost is a key issue and parallelisation of the computations must be efficient to reduce the elapsed time spent for the simulations. As pointed out earlier the amount of computation spent by ASIS to solve the chemical system can vary significantly from one grid point to another. This renders the equilibrium work balancing of tasks more difficult if a domain decomposition strategy is adopted to implement the parallelisation. As already discussed with the surface emissions, one possibility to diminish the number of iterations and the heterogeneity in the CPU used at each grid-point is to account for non chemical tendencies in the species continuity equations (term $F$ of Eq.4). Rather than updating the concentrations after each process the resulting tendencies could be added and integrated within ASIS. This strategy has been adopted for example by Menut et al. (2013) for the CHIMERE model, it remains to be seen if the stability and the positivity of the solution can be maintained.

The present version of the ASIS solver adresses the evolution of the concentrations in gas phase only. For some applications the aqueous phase associated with the presence of clouds must be also considered (e.g. Leriche et al. 2013). The chemistry module has to solve both gaseous and aqueous phases chemistry as well as mass transfer reactions between gas and liquid phases. There is a priori no difficulty to add the prognostic concentrations in the water phase to the system of equations and make a linearization similar to what is done in Eq. (6). However, the addition of aqueous reactions tend to increase the stiffness of the numerical ODE (Audiffren et al., 1998) so the performances of ASIS could diminish and may result in reduced timesteps and increased computer time.

In conclusion, the ASIS solver can deal with many situations encountered in modeling atmospheric chemistry for a computational cost affordable by CTMs and GCMs that include comprehensive chemical schemes. Evolution of ASIS solver to treat aqueous phase chemistry is planned in the near future.
The Fortran code to run the ASIS solver on the FLUX case described is section 3 is available from CERFACS. Requests to access the code can be addressed to D. Cariolle (cariolle@cerfacs.fr) as supplementary file to the present article and can be downloaded from the CERFACS server (www.cerfacs.fr). The ASIS code is property of the CERFACS and includes libraries that belong to other holders.

The code associated with the chemistry model includes subroutines that define the mechanism and those more specific to the ASIS solver. At this stage we have not developed an external driver or a pre-processor that would generate specific codes based on the adopted mechanism. This choice was done because our experience is that the maintenance of the driver outputs can be somewhat cumbersome when many developers work in parallel on a CTM. In addition, the code generated by the driver must be often optimized for the computer used and adapted to the CTM. It is therefore not used directly, which introduces further constraints on the maintenance of the overall code.

Our approach is rather to define the mechanism by a limited number of fortran subroutines that are simply added to the other routines of the code. The num_species routine names and numbers the species, the indices_reactions routine does the same for the reactions. The reactions are classified in 3 groups:

1/ A -> b B + c C
2/ A + A -> b B + c C
3/ a A + b B -> c C + d D

The first group includes photodissociations and thermal decomposition of the species. This classification is done in order to optimize the calculation of the terms of the matrix $M$ of Eq. (7). Some reactions gives more than 2 products and fractional sub-reactions must be introduced. For example the following reaction with fractional products:

$HC5P + NO3 \rightarrow 0.021 \times HCHO + 0.239 \times ALD + 0.828 \times KET + 0.699 \times HO2 + 0.040 \times MO2 + 0.262 \times ETHP + 0.391 \times XO2 + NO2$

will be decomposed in 4 sub-reactions within the indices_reactions routine:

$zloc2 = ZSPEC(1.0, JPHC5P, 1.0, JPNO3, 0.021, JPHCHO, 0.239, JPALD)$
$Zindice_4(JP4_HC5P_NO3_ii) = zloc2$
$zloc2 = ZSPEC(0.0, JPHC5P, 0.0, JPNO3, 0.828, JPKET, 0.699, JPHO2)$
$Zindice_4(JP4_HC5P_NO3_i) = zloc2$
$zloc2 = ZSPEC(0.0, JPHC5P, 0.0, JPNO3, 0.040, JPMO2, 0.262, JPETHP)$
$Zindice_4(JP4_HC5P_NO3_iiv) = zloc2$

paying attention not to duplicate associated fluxes.
Once the definition of species and reactions is completed, the calculation of the matrices (Eq. 7) is done by the \textit{fill\_matrix} routine, the timesteps are monitored by the \textit{define\_dt} routine and the \textit{resolution\_solution} of the linear systems by the \textit{Solvesys} routine.

\textit{Acknowledgements.} This work was supported by the Monitoring Atmospheric Composition and Climate (http://www.gmes-atmosphere.eu/) and COPERNICUS Atmospheric Monitoring Service (https://atmosphere.copernicus.eu/) E.U. projects. The authors thank Emanuele Emili, Andrea Piacentini and Michael Prather for their very helpful comments on the manuscript.
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