Definitions

symbol	description	unit
z	vertical coordinate	cm
ϵ_k	abundance of element k with respect to H	–
n_i	particle density of molecule i	cm^{-3}
$n_{\langle \mathrm{H} \rangle}$	total hydrogen nuclei density	cm^{-3}
$\rho = \sum_i n_i m_i = \mu_\mathrm{H}\, n_{\langle \mathrm{H} \rangle} = \mu \sum_i n_i$	gas mass density	$\mathrm{g\,cm}^{-3}$
m_i	mass of particle i	g
m_k	mass of element k	g
$\mu = \sum_i n_i m_i \Big/ \sum_i n_i$	mean gas particle mass	g
$\mu_\mathrm{H} = \sum_k \epsilon_k m_k$	proportionality constant	g
T	gas temperature	K
$p = \frac{\rho}{\mu} kT = \sum_i n_i\, kT$	gas pressure	$\mathrm{dyn\,cm}^{-2}$
D	diffusion coefficient	$\mathrm{cm}^2\,\mathrm{s}^{-1}$

1 The Atmospheric Diffusion Problem

To simultaneously model the evolution of the chemical composition of the atmosphere and the crust of a hot rocky planet, we use the implicit/explicit time-dependent second-order diffusion solver DIFFUSE developed by Peter Woitke. At the top of the atmosphere, a modified fixed-flux boundary condition will be applied to allow for the Jeans escape of H_2 and He (see Sect. 3.1), whereas at the bottom, a modified fixed-concentration boundary condition will be applied to treat the outgasing/deposition of elements from/to the crust (see Sect. 3.2). By book-keeping the element fluxed through the lower boundary, we can also predict how the crust composition changes with time.

In the planet atmosphere between these boundaries, we solve the second-order diffusion problem

$$\frac{\partial(n_{\langle \mathrm{H} \rangle}\, \epsilon_k)}{\partial t} + \nabla(\vec{v}\, n_{\langle \mathrm{H} \rangle} \epsilon_k) \;=\; \nabla\left(n_{\langle \mathrm{H} \rangle} D\, \nabla \epsilon_k\right) \;. \tag{1}$$

Assuming a 1-d plane-parallel and static ($\vec{v}=0$) atmosphere, the equations to solve are

$$\frac{d}{dt}\Big(n_{\langle \mathrm{H} \rangle}\, \epsilon_k\Big) \;=\; \frac{d}{dz}\left(n_{\langle \mathrm{H} \rangle} D\, \frac{d\epsilon_k}{dz}\right) \;. \tag{2}$$

Assuming, in addition, a constant density structure $n_{\langle \mathrm{H} \rangle} = n_{\langle \mathrm{H} \rangle}(z)$ the equations simplify to

$$\frac{d\epsilon_k}{dt} \;=\; \frac{1}{n_{\langle \mathrm{H} \rangle}}\, \frac{d}{dz}\left(n_{\langle \mathrm{H} \rangle} D\, \frac{d\epsilon_k}{dz}\right) \;, \tag{3}$$

where $\epsilon_k(z,t)$ are the height-dependent and time-dependent element abundances in the planet atmosphere we wish to determine. We note that $n_{\langle \mathrm{H} \rangle} = n_{\langle \mathrm{H} \rangle}(z)$ and $D = D(z)$ vary by many orders of magnitude throughout the atmosphere, often more than the element abundances we wish to determine, therefore we *cannot* neglect the $\frac{dn_{\langle \mathrm{H} \rangle}}{dz}$ and $\frac{dD}{dz}$ terms as

$$\frac{d\epsilon_k}{dt} \;\neq\; D\, \frac{d^2\epsilon_k}{dz^2} \;. \tag{4}$$

The diffusion constant $D(z)$ is determined by (i) the microscopic diffusion which turns out to be important in the uppermost layers D_micro, and (ii) the turbulent quasi-diffusion D_mix due to vertical mixing processes excited e.g. by convective or other flow instabilities.

$$D(z) = D_\mathrm{micro}(z) + D_\mathrm{mix}(z) \tag{5}$$

Since the turbulent diffusion takes place on large spatial scales, we can safely assume that $D_{\rm mix}$ does not depend on the molecule (or element) we want to diffuse. Concerning $D_{\rm micro}$, however, there is a small dependence on the size and reduced mass of the molecule with respect to collisions with H_2, see Woitke & Helling (2003, Eq. (26) therein), which causes deviations of D as function of molecule by a factor of about 2 to 3. We will simply neglect these deviations in the following.

This neglection allows us to calculate the diffusion of elements rather than the diffusion of individual molecules. The total particle density [cm^{-3}] of element k is given by

$$n_{\langle\rm H\rangle}\,\epsilon_k = \sum_i s_{i,k}\,n_i \tag{6}$$

where $s_{i,k}$ is the stoichiometic factor of element k in molecule i, for example $s_{\rm H_2O,H} = 2$. Using Eq. (2), the diffusion of that total nuclei particle density is given by

$$\begin{aligned}
\frac{d}{dt}\left(n_{\langle\rm H\rangle}\,\epsilon_k\right) &= \frac{d}{dt}\sum_i s_{i,k}\,n_i \;=\; \sum_i s_{i,k}\,\frac{dn_i}{dt} && (7)\\
&= \sum_i s_{i,k}\,\frac{d}{dz}\left(n_{\langle\rm H\rangle} D\,\frac{d}{dz}\left(\frac{n_i}{n_{\langle\rm H\rangle}}\right)\right) && (8)\\
&= \frac{d}{dz}\left(n_{\langle\rm H\rangle} D\,\frac{d}{dz}\left(\sum_i s_{i,k}\frac{n_i}{n_{\langle\rm H\rangle}}\right)\right) && (9)\\
&= \frac{d}{dz}\left(n_{\langle\rm H\rangle} D\,\frac{d\epsilon_k}{dz}\right) && (10)
\end{aligned}$$

2 Spatial Grid and Initial Conditions

We use an equidistant grid in $\{z_i\,|\,i=0,...,I\}$ to discretise the 1d-structure of the planetary atmosphere with fixed temperature and pressure points in hydrostatic equilibrium, $T_i = T(z_i)$ and $p_i = p(z_i)$. At the lower boundary ($z_0 = 0$) of the model, the atmospheric gas is in physical contact with the crust. The crust is represented by column densities $N_j^{\rm cond}$ for a number of $j = 1,...,J$ condensed species.

At initialisation ($t = 0$), we consider a set of total (gas plus condensed) element abundances $\{\epsilon_k^0\}$ at temperature T_0 and pressure p_0 in phase equilibrium, using the GGchem-code (Woitke et al., 2017). The total element abundances $\{\epsilon_k^0\}$ are chosen from one of the sets listed in Table 1. The results of this phase equilibrium computation are

- the identification and number J of simultaneously present condensates
- the volume density of units of the condensed species $n_j^{\rm cond}$ ($j = 1,...,J$) [cm^{-3}],
- the element abundances $\{\epsilon_k^{\rm gas}\}$ in the gas above the condensates

We define the condensed element abundances as

$$n_{\langle\rm H\rangle}\,\epsilon_k^{\rm cond} = \sum_{j=1}^{J} s_{j,k}\,n_j^{\rm cond} \tag{11}$$

where $s_{j,k}$ is the stoichiometric factor of element k in condensate j, for example $s_{\rm Al_2O_3,O} = 3$. The element conservation is then given by

$$\epsilon_k^0 = \epsilon_k^{\rm gas} + \epsilon_k^{\rm cond}\ . \tag{12}$$

At initialisation, we fill the lowest atmospheric cell with element composition $\epsilon_k^{\rm gas}$, and use the identification and ratio of condensed species in phase equilibrium with that gas to initialise the

Table 1: Different sets of element abundances normalised to hydrogen (need citations). $A(-B)$ means $A \times 10^{-B}$.

	solar	Earth crust	meteoritic
H	1.00(+0)	1.00(+0)	1.00(+0)
He	8.51(−2)	1.08(−6)	–
Li	1.12(−11)	2.07(−3)	1.03(−5)
C	2.69(−4)	1.20(−2)	5.25(−2)
N	6.76(−5)	9.76(−4)	4.20(−3)
O	4.90(−4)	2.07(+1)	1.05(+0)
Na	1.74(−6)	7.39(−1)	1.00(−2)
Mg	3.98(−5)	6.90(−1)	2.07(−1)
Al	2.82(−6)	2.20(+0)	1.42(−2)
Si	3.24(−5)	7.23(+0)	2.09(−1)
P	2.57(−7)	2.44(−2)	1.49(−3)
S	1.32(−5)	7.86(−3)	5.24(−2)
Cl	3.16(−7)	2.94(−3)	4.38(−4)
K	1.07(−7)	3.85(−1)	7.52(−4)
Ca	2.19(−6)	7.45(−1)	1.15(−2)
Ti	8.91(−8)	8.42(−2)	4.74(−4)
Cr	4.37(−7)	1.41(−3)	2.42(−3)
Mn	2.69(−7)	1.24(−2)	2.06(−3)
Fe	3.16(−5)	7.26(−1)	1.65(−1)
Ni	1.66(−6)	1.03(−3)	9.30(−3)

crust. At given pressure, there is a free constant in phase equilibrium, namely the total amount of condensates. We can add an arbitrary amount of the mixture of condensates as

$$\widetilde{\epsilon}_k^{\,0} = \epsilon_k^{\rm gas} + X\,\epsilon_k^{\rm cond}\ . \tag{13}$$

and re-run the phase equilibrium computation at the same pressure and temperature, but now with $\{\widetilde{\epsilon}_k^{\,0}\}$ instead of $\{\epsilon_k^0\}$ – all resulting gas properties including $\epsilon_k^{\rm gas}$ will stay the same. This property of phase equilibrium allows us to consider the "thickness of the active crust" D as a free parameter. The initial column densities in the active crust are given by

$$N_j^{\rm cond} = D\,n_j^{\rm cond} \tag{14}$$

All atmospheric cells above the bottom cell ($i = 1, ..., I$) are finally filled with a gas of solar abundances, or any other chosen set of element abundances.

3 Boundary Conditions

3.1 Upper boundary condition

We specify the escaping element fluxes from the top of the atmosphere by applying the formula for Jeans escape → Tian (2015) as upper boundary condition of the model.
Where to apply that formula? → exobase → Volkov et al. (2011).
Here, we need to decompose the elements into molecules, apply the Jeans escape to each molecule, and lump the escaping fluxes together to get the escaping element fluxes.

3.2 Lower boundary condition

At the bottom of the atmosphere, the atmospheric gas is in physical contact with the crust. At pressures of the order of a few tenth of a bar to several bars, the collision rates of gas particles with the crust are huge, leading to a fast relaxation towards phase equilibrium. We will therefore assume that the gas at the bottom of the atmosphere is saturated (i.e. in phase equilibrium) with respect to the solid/liquid materials present in the crust.

$$S_j(\epsilon_k)\Big|_{z=0} \;=\; 1 \tag{15}$$

As shown in Appendix B of (Woitke et al., 2017), the number of simultaneously present condensates in phase equilibrium J is limited by the number of elements K contained in them,

$$\begin{aligned} J &= \text{number of condensates in crust } j = 1, ..., J \\ K &= \text{number of condensed elements in crust } k = 1, ..., J, J+1, ..., K \end{aligned}$$

i.e. the number of condensing elements can (and usually will) exceed the number of condensates in the crust ($K \geq J$). To formulate the phase equilibrium inner boundary condition for the diffusion experiment, we would need to solve J equations (Eq. 15) for K elements which, however, is not possible if $K > J$. In order to solve this problem, we make a case differentiation between "limiting" and "non-limiting" elements, and use the element stoichiometry of the consensates in the crust as an additional constraint. Our inner boundary condition is formulated as follows:

$$\begin{array}{lcl} \text{1) element not affected by condensation} & : & \text{zero-flux boundary condition } j_k = 0, \\ \text{2) limiting element} & : & \text{fixed concentration } \epsilon_k \text{ from Eq. (15)}, \\ \text{3) non-limiting element} & : & \text{derived element flux } j_k \neq 0 \;\; . \end{array} \tag{16}$$

In order to compute the fluxes j_k of the non-limiting elements, we first run the diffusion solver for the limiting elements with fixed ϵ_k boundary condition, which results in the fluxes of the limiting elements through the inner boundary:

$$\text{limiting element } k = 1, ..., J\text{:} \qquad j_k = -n_{\langle\mathrm{H}\rangle} D \frac{d\epsilon_k}{dz}\Big|_{z=0} \; . \tag{17}$$

Next, we reconstruct the changes of the crust column densities $N_j^{\rm cond}$ from these fluxes by solving the following system of linear equations

$$\sum_{j=1}^{J} s_{j,k} \frac{dN_j^{\rm cond}}{dt} \;=\; j_k \;, \tag{18}$$

which are J equations for J unknowns. Finally, we derive the non-limiting element fluxes by using the stoichiometry of the crust condensates

$$\text{non-limiting element } k = J+1, ..., K\text{:} \qquad j_k = \sum_j s_{j,k} \frac{dN_j^{\rm cond}}{dt} \tag{19}$$

For example, let's assume we have $MgSiO_3$[s] and Mg_2SiO_4[s] as condensates ($J = 2$), which are made of elements Mg, Si and O ($K = 3$). The least abundant elements in the gas phase will limit the growth of these condensates, here Mg and Si, whereas there is plenty of O available, so there is one non-limiting element, namely O. Applying the condition of phase equilibrium at the bottom of the atmosphere, we calculate the element abundances $\epsilon_{\rm Mg}$ and $\epsilon_{\rm Si}$ in phase equilibrium over the crust, and use these values as boundary conditions for the diffusion solver. As a result, the element fluxes through the inner boundary $j_{\rm Mg}$ and $j_{\rm Si}$ are determined via Eq. (17). To calculate the respective changes of crust column densities, we solve

$$\begin{pmatrix} 1 & 2 \\ 1 & 1 \end{pmatrix} \begin{pmatrix} dN^{\rm cond}_{\rm MgSiO_3}/dt \\ dN^{\rm cond}_{\rm Mg_2SiO_4}/dt \end{pmatrix} = \begin{pmatrix} j_{\rm Mg} \\ j_{\rm Si} \end{pmatrix} \tag{20}$$

for the unknowns $dN^{\rm cond}_{\rm MgSiO_3}/dt$ and $dN^{\rm cond}_{\rm Mg_2SiO_4}/dt$. Finally the matching oxygen flux through the inner boundary is found from the stoichiometry of the crust condensates as

$$j_{\rm O} \;=\; 3\,\frac{dN^{\rm cond}_{\rm MgSiO_3}}{dt} + 4\,\frac{dN^{\rm cond}_{\rm Mg_2SiO_4}}{dt} \tag{21}$$

which, in the last step, is then used as boundary condition to simulate the diffusion of oxygen in the atmosphere.

This inner phase-equilibrium boundary condition (Eq. 16) can be used to simulate the deposit of new condensates on top of the crust as well as the outgasing of crust materials into the atmosphere. It can also be used for mixed cases, where for example one condensate outgases wheras, at the same time, other condensates grow on top of the crust.

3.3 Updating the crust thickness and composition

The diffusion experiment as described in Sections (3.1) and (3.2) is carried out for a timestep Δt during which the crust column densities $N^{\rm cond}_j$ change, but we assume that the selection of crust composition does not change substantially. However, this is not required in general. After each time step we first invert and then redo the procedure as discibed in Sect. 2.

In the first step, we decompose all condensates in the active crust and all molecules in the lowest atmospheric cell into elements as

$$N_k = n_{\langle{\rm H}\rangle}\epsilon^{\rm gas}_k * \Delta z + \sum_{j=1}^{J} s_{j,k} N^{\rm cond}_j \;, \tag{22}$$

where Δz is the thickness of the lowest atmospheric cell and the N_k are element column densities in crust and lowest cell. We “load” these

$$\epsilon^0_k = N_k/N_{\rm H} \tag{23}$$

4 Element Conservation

References

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