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	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	dyn cm^{-2}
D	diffusion coefficient	cm^2 s^{-1}

<div align="center">Definitions</div>

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

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

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_{mix} does not depend on the molecule (or element) we want to diffuse. Concerning D_{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 $[\mathrm{cm}^{-3}]$ of element k is given by

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

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

$$\frac{d}{dt} \left(n_{\langle H \rangle} \, \epsilon_k \right) \;=\; \frac{d}{dt} \sum_i s_{i,k} \, n_i \;=\; \sum_i s_{i,k} \frac{dn_i}{dt} \tag{7}$$

$$= \; \sum_i s_{i,k} \frac{d}{dz} \left(n_{\langle H \rangle} D \frac{d}{dz} \left(\frac{n_i}{n_{\langle H \rangle}} \right) \right) \tag{8}$$

$$= \; \frac{d}{dz} \left(n_{\langle H \rangle} D \frac{d}{dz} \left(\sum_i s_{i,k} \frac{n_i}{n_{\langle H \rangle}} \right) \right) \tag{9}$$

$$= \; \frac{d}{dz} \left(n_{\langle H \rangle} D \frac{d\epsilon_k}{dz} \right) \tag{10}$$

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, $T(z_i)$ and $p(z_i)$. At the lower boundary ($z = 0$) of the model, the atmospheric gas is in contact with the crust. The crust is represented by column densities N_j^{cond} for a number of $j = 1, ..., J$ condensed species.

At initialisation ($t = 0$), we consider one set of total (gas and condensed) element abundances $\{\epsilon_k^0\}$ at temperature $T(z = 0)$ and pressure $p(z = 0)$ 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 number of simultaneously present condensates J,
- the selection of condensates,
- the volume density of units of the condensated species n_j^{cond} ($j = 1, ..., J$) $[\mathrm{cm}^{-3}]$,
- the element abundances $\{\epsilon_k^{\mathrm{gas}}\}$ of the gas above the condensates

We define the condensed element abundances as

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

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

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

At initialisation, we fill the lowest atmospheric cell with element composition $\epsilon_k^{\mathrm{gas}}$, and use the selection and ratio of condensed species to initialise the crust. There is one free constant in 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)

phase equilibrium computations, namely the total amount of condensates. If we add an arbitrary amount of our mixture of condensates as

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

and re-run the phase equilibrium computation for the same pressure and temperature, but now with $\{\widetilde{\epsilon}_k^0\}$ instead of $\{\epsilon_k^0\}$, all resulting gas properties including $\epsilon_k^{\mathrm{gas}}$ 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

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

All atmospheric cells above the bottom cell ($i = 2, ..., I$) are finally filled with gas of solar abundances, or any other chosen atmospheric gas 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 contact with the crust. At pressures between fractions 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 (is in phase equilibrium) with respect to the solid/liquid materials present in the crust.

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

As shown in Appendix B of (Woitke et al., 2017), the number J of simultaneously present condensates in phase equilibrium is limited and cannot exceed the number of elements K contained in them,

$$
\begin{aligned}
J &= \text{number of condensates in crust } j = 1, ..., J \\
K &= \text{number of condensed elements in crust } k = 1, ..., K \\
J &\leq K \\
N &= K - J \geq 0 \text{ number of non-limiting elements,}
\end{aligned}
$$

i.e. the number of condensing elements can (and usually will) exceed the number of condensates in the crust. In oder to formulate the inner boundary condition for the diffusion experiment, we need to solve J equations (Eq. 15) for K elements which is not possible if $N < K$. In order to solve this problem, we need to make a case differentiation and use the element stoichiometry of the consensates to formulate our inner boundary condition as follows

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

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 boundary element fluxes

$$\text{limiting element } k = 1, ..., J: \qquad j_k = -n_{\langle H \rangle} D \frac{d\epsilon_k}{dz}\Big|_{z=0} \ . \qquad (16)$$

Next, we reconstruct the changes of crust column densities N_j^{cond} from the limiting element boundary fluxes by the following system of linear equation equations

$$\sum_j s_{j,k} \frac{dN_j^{\mathrm{cond}}}{dt} = j_k \qquad (17)$$

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

$$\text{non-limiting element } k = J+1, ..., K: \qquad j_k = \sum_j s_{j,k} \frac{dN_j^{\mathrm{cond}}}{dt} \qquad (18)$$

3.3 Updating the crust thickness and composition

4 Element Conservation

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