

# Diffusion and Gravitational De-mixing in Disks

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## 1 Chemistry with Diffusion

The basic rate equation to solve for each chemical species is

$$\frac{\partial n_i}{\partial t} = P_i - L_i - \frac{\partial \Phi_i}{\partial z}, \quad (1)$$

where  $n_i$  [ $\text{cm}^{-3}$ ] is the particle density,  $P_i$  and  $L_i$  [ $\text{cm}^{-3}\text{s}^{-1}$ ] are the chemical production and loss rates, and  $\Phi_i$  [ $\text{cm}^{-2}\text{s}^{-1}$ ] is the diffusive particle flux according to [Hu et al. \(2012\)](#), [Zahnle et al. \(2016\)](#) and [Rimmer & Helling \(2016\)](#)

$$\Phi_i = -(K + D_i) n \frac{\partial}{\partial z} \left( \frac{n_i}{n} \right) + D_i n_i \frac{(\mu - m_i) g}{kT}, \quad (2)$$

where  $n = \sum_i n_i$  is the total particle density,  $m_i$  the mass of a gas particle of kind  $i$  and  $\mu = \sum n_i m_i / n$  the mean molecular weight. We have neglected the “thermal diffusion factor”  $\alpha_T$  here, which describes a second-order effect that the lightest molecules tend to diffuse towards the warmest places. Using the ideal gas law  $p = nkT$ , assuming a hydrostatic structure  $-\frac{d \ln p}{dz} = \frac{1}{H} = \frac{\mu g}{kT}$ , and using abbreviation  $\frac{1}{H_i} = \frac{m_i g}{kT}$ , one can show that Eq. (2) can alternatively be written as

$$\Phi_i = -K \left[ \frac{\partial n_i}{\partial z} + n_i \left( \frac{1}{H} + \frac{1}{T} \frac{dT}{dz} \right) \right] - D_i \left[ \frac{\partial n_i}{\partial z} + n_i \left( \frac{1}{H_i} + \frac{1}{T} \frac{dT}{dz} \right) \right]. \quad (3)$$

$K$  [ $\text{cm}^2/\text{s}$ ] is the eddy-diffusion coefficient caused by large-scale turbulent mixing motions in the  $z$ -direction, sometimes also denoted by  $k_{zz}$ .  $K$  is generally given by a characteristic mixing velocity times a characteristic length

$$K = \langle v_z \rangle L, \quad (4)$$

where  $L$  is the size of the largest eddy (“mixing length”) and  $\langle v_z \rangle$  is the root-mean square of the fluctuating part of the vertical gas velocities. According to the  $\alpha$ -disk model of [Shakura & Sunyaev \(1973\)](#), the typical vertical length scale is  $L \approx H$  and the turbulent mixing velocity is approximated as  $\langle v_z \rangle \approx \alpha_{\text{mix}} c_s$ , thus

$$K = \alpha_{\text{mix}} c_s H, \quad (5)$$

where  $c_s = \sqrt{kT/\mu}$  is the local isothermal sound speed and  $T$  the temperature. Typical values used in the literature are  $\alpha_{\text{mix}} \approx 10^{-5} \dots 10^{-2}$ . In contrast, the gas-kinetic micro-physical diffusion coefficient  $D_i$  [ $\text{cm}^2\text{s}^{-1}$ ], due to Brownian motions,

$$D_i = \frac{1}{3} \frac{v_{\text{th},i}}{\sigma_{ia} n} \quad (6)$$

depends on species  $i$  because the collisional cross section  $\sigma_{ia}$  depends on the “sizes” of both  $i$  and collision partner  $a$ , and the relative velocity depends on the reduced mass. A simple hard-sphere approximation would be ([Jeans, 1967](#))

$$D_i = \frac{1}{3} \left( \sum_j \frac{n_j \pi (r_i + r_j)^2}{\sqrt{\frac{8kT}{\pi m_{\text{red}}}}} \right)^{-1} = \frac{1}{3} \sqrt{\frac{8kT}{\pi m_i}} \left( \sum_j \frac{n_j \pi (r_i + r_j)^2}{\sqrt{1 + \frac{m_i}{m_j}}} \right)^{-1} = \frac{b_{ia}}{n}, \quad (7)$$

where the effective radii of the molecules  $r_i$  can be measured from viscosity experiments ([Jeans, 1967](#)), or calculated from Lennard-Jones potentials<sup>1</sup>.  $b_{ia}$  is called the binary diffusion coefficient [ $\text{cm}^{-1}\text{s}^{-1}$ ] for collisions between species  $i$  and a “background atmosphere” denoted by  $a$ .

<sup>1</sup>see e.g. <https://demonstrations.wolfram.com/BinaryDiffusionCoefficientsForGases/>

Table 1: Molecular radii for diffusion coefficients calculated with <sup>1</sup> at  $T=300$  K

particle $i$	radius $r_i$
He	1.084 Å
H <sub>2</sub>	1.366 Å
O <sub>2</sub>	1.811 Å
CO	1.886 Å
N <sub>2</sub>	1.901 Å
CH <sub>4</sub>	2.075 Å
H <sub>2</sub> O	2.178 Å
CO <sub>2</sub>	2.304 Å

I do not fully understand the second term in Eq. (2), but it seems to me that it has been reverse-engineered from the observed fact that, in carefully prepared diffusion experiments, the heavy gases eventually only populate the bottom of the chamber (such as bromine gas Br<sub>2</sub>) whereas the light gases tend to also populate the top. This agrees well with our daily experience that light gases like He or H<sub>2</sub> ascend in the atmosphere, making balloons fly (buoyancy). According to private communication with Kevin Zahnle, 2019, the original derivation of Eq. (2) can be found in [Hunten \(1973\)](#) with further reading in [Kuramoto et al. \(2013\)](#), but I must admit that I don't understand these papers.

In order to verify that behaviour, let us examine the case of a non-reactive ( $P_i = L_i = 0$ ) mixture of ideal gases without mixing ( $K \rightarrow 0$ ) in equilibrium, where both  $n(z)$  and  $n_i(z)$  become time-independent functions of  $z$  only. The diffusive fluxes vanish and we find

$$\begin{aligned}
 \Phi_i = 0 &= -D_i n \frac{d}{dz} \left( \frac{n_i}{n} \right) + D_i n_i \frac{(\mu - m_i) g}{kT} \\
 \Rightarrow \frac{n}{n_i} \frac{d}{dz} \left( \frac{n_i}{n} \right) &= \frac{(\mu - m_i) g}{kT} \\
 \Rightarrow \frac{d}{dz} \ln \frac{n_i}{n} &= \frac{d}{dz} \ln \frac{p_i}{p} = \frac{(\mu - m_i) g}{kT} \\
 \Rightarrow \ln \frac{p_i}{p} \Big|_0^z &= z \frac{(\mu - m_i) g}{kT} = \frac{z}{H} - \frac{z}{H_i} \\
 \Rightarrow p_i(z) &= p_i(0) \exp \left( -\frac{z}{H_i} \right) \quad \text{and} \quad p(z) = p(0) \exp \left( -\frac{z}{H} \right)
 \end{aligned}$$

Thus, the atmosphere  $a$  and the selected species  $i$  follow their own hydrostatic structure with pressure scale heights  $H = kT/(\mu g)$  and  $H_i = kT/(m_i g)$ . When considering e.g. H<sub>2</sub> in a CH<sub>4</sub>-atmosphere, where the scale heights are different by a factor of 8, going 5 scale heights upwards means to increase the H<sub>2</sub>-concentration by a factor of about 80. In contrast, if we include strong turbulent mixing  $K \gg D_i$ , then the dominating term for the diffusive flux is  $\Phi_i = -K n \frac{d}{dz} \left( \frac{n_i}{n} \right) = 0$ , which ensures that the concentration  $n_i/n$ , in our case the H<sub>2</sub>/CH<sub>4</sub>-ratio, remains constant as function of height.

## 2 Element Abundances

An important question is in how far the element abundances in the disc could be affected by diffusive transport and become spatially dependent quantities. If the answer to that question is yes, then how and where should we set them as initial or boundary conditions as parameters in our models?

The element abundances are given by

$$n_{\langle\text{H}\rangle} \epsilon_k = \sum_i s_{i,k} n_i \quad (8)$$

where  $s_{i,k}$  are the stoichiometric factors,  $\epsilon_k$  are the element abundances with respect to hydrogen, and  $n_{\langle\text{H}\rangle}$  is the total hydrogen nuclei particle density. The changes of the element abundances follow from Eq. (8) after multiplication with  $s_{i,k}$  and summation over all chemical species

$$\frac{\partial}{\partial t} (n_{\langle\text{H}\rangle} \epsilon_k) = \sum_i s_{i,k} (P_i - L_i) - \sum_i \frac{\partial}{\partial z} (s_{i,k} \Phi_i) . \quad (9)$$

Chemical reactions conserve the element abundances, hence the first term in Eq. (9) vanishes. Concerning the diffusive flux  $\Phi_i$  [ $\text{cm}^{-2}\text{s}^{-1}$ ] let us first consider the case  $K \gg D_i$  where turbulent mixing dominates

$$\Phi_i = -K n \frac{\partial}{\partial z} \left( \frac{n_i}{n} \right) . \quad (10)$$

The element fluxes are then given by

$$\Phi_k = \sum_i s_{i,k} \Phi_i = - \sum_i s_{i,k} K n \frac{\partial}{\partial z} \left( \frac{n_i}{n} \right) \quad (11)$$

$$= -K n \frac{\partial}{\partial z} \left( \frac{\sum_i s_{i,k} n_i}{n} \right) \quad (12)$$

$$= -K n \frac{\partial}{\partial z} \left( \frac{n_{\langle\text{H}\rangle} \epsilon_k}{n} \right) , \quad (13)$$

where we have used that  $K$  does not depend on molecule. Equation. (9) can hence be written as

$$\frac{\partial}{\partial t} (n_{\langle\text{H}\rangle} \epsilon_k) = - \frac{\partial}{\partial z} \Phi_k . \quad (14)$$

Equation (13) states that *eddy diffusion always works against spacial gradients of element abundances*. No matter how complicate the chemical processes are, eddy diffusion will tend to diminish such gradients ( $\Phi_k \rightarrow 0$ ), making sure that, on the long run, the element abundances become constant throughout the disc<sup>2</sup>.

Although this seems rather straightforward, there are papers which argue that mixing could change the element abundances. For example, when only one particular molecule is considered, which is abundant say deep in the disk, and it is mixed upwards where it dissociates, one would expect this process to enrich the higher layers with the elements the molecule was composed of. However, this is not how eddy mixing works. Mixing only *exchanges* molecules for other molecules

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<sup>2</sup>Precisely speaking, this statement is correct only when  $n_{\langle\text{H}\rangle}(z) \propto n(z)$ . Since  $\rho = \mu_{\text{H}} n_{\langle\text{H}\rangle}$  (mass density) and  $p = nkT = \rho kT/\mu$  (pressure), we have

$$\frac{\partial}{\partial z} \left( \frac{n_{\langle\text{H}\rangle} \epsilon_k}{n} \right) = \frac{\partial}{\partial z} \left( \frac{n_{\langle\text{H}\rangle}}{n} \right) \epsilon_k + \frac{n_{\langle\text{H}\rangle}}{n} \frac{\partial \epsilon_k}{\partial z} = \frac{\partial}{\partial z} \left( \frac{\mu}{\mu_{\text{H}}} \right) \epsilon_k + \frac{n_{\langle\text{H}\rangle}}{n} \frac{\partial \epsilon_k}{\partial z} .$$

If we can neglect the first term we find

$$\Phi_k = -K n_{\langle\text{H}\rangle} \frac{\partial \epsilon_k}{\partial z} .$$

This complication, which can be expected to be relevant close to the main phase transitions  $\text{H}^+ \rightarrow \text{H}$  and  $\text{H} \rightarrow \text{H}_2$  may or may not be related to the so-called ‘‘thermal diffusion factor’’  $\alpha_T$  which is included in the basic equation of Zahnle et al. (2016) and Rimmer & Helling (2016) as

$$\Phi_i = -(K + D_i) n \frac{\partial}{\partial z} \left( \frac{n_i}{n} \right) + D_i n_i \left( \frac{(\mu - m_i) g}{kT} - \frac{\alpha_T}{T} \frac{dT}{dz} \right) ,$$

but has been neglected here. This is bugging me. I just don’t understand it at the moment.

from the neighbourhood, and if you properly sum up the total effect on the element abundances, via  $\Phi_k = \sum_i s_{i,k} \Phi_i$ , the net effect is zero, unless there is a spatial gradient in element abundances in the first place, in which case eddy diffusion will reduce that gradient.

That being said, however, the conclusions above are only valid as long as  $K$  is independent of molecules/particle to be mixed by diffusion. Once we add  $D_i$  with  $D_i \gtrsim K$  (above the *homopause*), we can no longer pull out the net diffusion coefficient ( $K + D_i$ ) from the sum in Eq. (13). In that case, diffusion *can* change the element abundances. This becomes even more relevant when the last term in Eq. (2), driven by gravity, is considered. If that term dominates, a vertical structure will be established in which the light molecules and atoms are more abundant than heavy molecules in the uppermost layers. I would propose to call this effect *gravitational de-mixing*, because it is driven by gravity (caused by the different particle masses) and needs to overcome diffusive mixing which tends to smooth out concentration gradients.

### 3 Solving chemistry with mixing

Hu et al. (2012), see also Rimmer & Helling (2016) with erratum Rimmer & Helling (2019), formulate the 1D reaction-diffusion problem in the following way. Let us consider height grid points  $\{z_j \mid j = 1, \dots, J\}$ . The basic reaction-diffusion equation can then be numerically discretised as

$$\frac{\partial n_{i,j}}{\partial t} = P_{i,j} - L_{i,j} - \frac{\Phi_{i,j+1/2} - \Phi_{i,j-1/2}}{z_{j+1/2} - z_{j-1/2}}, \quad (15)$$

where the notation means  $x_{j\pm 1/2} = \frac{1}{2}(x_j + x_{j\pm 1})$ , and

$$\begin{aligned} \Phi_{i,j+1/2} &= -(K_{j+1/2} + D_{i,j+1/2}) n_{j+1/2} \frac{\frac{n_{i,j+1}}{n_{j+1}} - \frac{n_{i,j}}{n_j}}{z_{j+1} - z_j} \\ &\quad + D_{i,j+1/2} \frac{1}{2} (n_{i,j} + n_{i,j+1}) \frac{(\mu_{j+1/2} - m_i) g_{j+1/2}}{kT_{j+1/2}} \end{aligned} \quad (16)$$

$$\begin{aligned} \Phi_{i,j-1/2} &= -(K_{j-1/2} + D_{i,j-1/2}) n_{j-1/2} \frac{\frac{n_{i,j}}{n_j} - \frac{n_{i,j-1}}{n_{j-1}}}{z_j - z_{j-1}} \\ &\quad + D_{i,j-1/2} \frac{1}{2} (n_{i,j} + n_{i,j-1}) \frac{(\mu_{j-1/2} - m_i) g_{j-1/2}}{kT_{j-1/2}} \end{aligned} \quad (17)$$

Assuming that all quantities are constant except for  $n_{i,j-1}$ ,  $n_{i,j}$  and  $n_{i,j+1}$  we write

$$-\frac{\Phi_{i,j+1/2} - \Phi_{i,j-1/2}}{z_{j+1/2} - z_{j-1/2}} = \mathcal{A} n_{i,j+1} + \mathcal{B} n_{i,j} + \mathcal{C} n_{i,j-1} \quad (18)$$

with

$$\mathcal{A} = \frac{1}{z_{j+1/2} - z_{j-1/2}} \left( + (K_{j+1/2} + D_{i,j+1/2}) \frac{n_{j+1/2}}{n_{j+1}(z_{j+1} - z_j)} - D_{i,j+1/2} \frac{1}{2} \frac{(\mu_{j+1/2} - m_i) g_{j+1/2}}{kT_{j+1/2}} \right) \quad (19)$$

$$\begin{aligned} \mathcal{B} &= \frac{1}{z_{j+1/2} - z_{j-1/2}} \left( - (K_{j+1/2} + D_{i,j+1/2}) \frac{n_{j+1/2}}{n_j(z_{j+1} - z_j)} - D_{i,j+1/2} \frac{1}{2} \frac{(\mu_{j+1/2} - m_i) g_{j+1/2}}{kT_{j+1/2}} \right. \\ &\quad \left. - (K_{j-1/2} + D_{i,j-1/2}) \frac{n_{j-1/2}}{n_j(z_j - z_{j-1})} + D_{i,j-1/2} \frac{1}{2} \frac{(\mu_{j-1/2} - m_i) g_{j-1/2}}{kT_{j-1/2}} \right) \end{aligned} \quad (20)$$

$$\mathcal{C} = \frac{1}{z_{j+1/2} - z_{j-1/2}} \left( + (K_{j-1/2} + D_{i,j-1/2}) \frac{n_{j-1/2}}{n_{j-1}(z_j - z_{j-1})} + D_{i,j-1/2} \frac{1}{2} \frac{(\mu_{j-1/2} - m_i) g_{j-1/2}}{kT_{j-1/2}} \right) \quad (21)$$

A straightforward idea to solve Eq. (15), in an iterative way, would be to consider  $n_{i,j+1}$  and  $n_{i,j-1}$  as given (determined by the previous downward sweep of chemistry and heating & cooling balance). In that case we could solve

$$\frac{\partial n_i}{\partial t} = \tilde{P}_i - \tilde{L}_i, \quad (22)$$

where

$$\tilde{P}_i = P_i + \mathcal{A} n_{i,j+1} + \mathcal{C} n_{i,j-1} \quad (23)$$

$$\tilde{L}_i = L_i - \mathcal{B} n_{i,j} . \quad (24)$$

The contribution of diffusive mixing to the production of species  $i$  on grid point  $j$  would be a constant “spontaneous” rate (with no entries into the Jacobian) whereas the respective loss rate would be proportional to  $n_{i,j}$ .

$$\text{“Mixing In”, type MI :} \quad \longrightarrow \quad \text{mol} \quad \text{rate constant } k = \mathcal{A} n_{i,j+1} + \mathcal{C} n_{i,j-1} \quad (25)$$

$$\text{“Mixing Out”, type MO :} \quad \text{mol} \quad \longrightarrow \quad \text{rate constant } k = \mathcal{B} \quad (26)$$

Both rates, regarded in isolation, violate the principle of element conservation, so we have to by-pass some of the automatic checks in PRODIMO.

### 3.1 Boundary condition

We apply zero-flux boundary conditions at  $j = 1$  and  $j = J$

$$\Phi_{i,1/2} = \Phi_{i,J+1/2} = 0 \quad (27)$$

In practise, this means that all terms in Eqs. (19) to (21) with  $K_{j-1/2}$  or  $D_{i,j-1/2}$  are dropped at  $j = 1$ , and all terms with  $K_{j+1/2}$  or  $D_{i,j+1/2}$  are dropped at  $j = J$ . For the pre-factor, we approximate  $z_{j+1/2} - z_{j-1/2} \approx z_2 - z_1$  at  $j = 1$  and  $z_{j+1/2} - z_{j-1/2} = z_J - z_{J-1}$  at  $j = J$ .

### 3.2 Current Implementation

Activate the mixing in PRODIMO by setting  $\alpha_{\text{mix}} > 0$  (e.g. `alpha_mix = 0.01`) in `Parameter.in`. The current implementation only has the eddy-diffusion included ( $K$ ) but not the molecular diffusion ( $D_i$ ). At initialisation, PRODIMO automatically creates the “MI” and “MO” reactions for all species. During the very first global iteration (with `restart = .false.`), when the chemical concentrations are not yet known, the mixing rates are ignored. From the second global iteration onwards, the MI rates are computed from the chemical concentrations stored in `nmol(:,ix,iz - 1)` and `nmol(:,ix,iz + 1)`. Because of the outward-downward direction of the chemistry sweep in PRODIMO, the concentrations from above are always from this global iteration, whereas the concentrations from below are taken from the previous global iteration. This means that the downward diffusion converges sooner than the upward diffusion. The upward diffusion is expected to converge no sooner than the number of gridpoints it has to cross, so if we consider a  $100 \times 100$  model, we expect to need about 100 global iterations.

As the current implementation only has eddy-diffusion (also applied to ice species), we can still assume that the element abundances are constant throughout the disk, so no changes required here.

## 4 Example Results

Figure 1 shows some first results. We see  $\text{H}_2$  being mixed up by eddy-diffusion into the optically thin regions, which triggers the production of OH and  $\text{H}_2\text{O}$  with peak-concentrations around  $N_{(\text{H})} \approx 10^{19} \text{ cm}^{-2}$ , higher than in models without mixing. Figure 2 shows that  $\text{H}_2$  is mostly photodissociated there, but partly also converted into  $\text{OH}^+$  via reactions with  $\text{O}^+$ . Further ion-neutral and recombination reactions, first with  $\text{H}_2$ , then with  $e^-$ , lead to the production of OH and  $\text{H}_2\text{O}$ . OH is then mostly photodissociated, but collisions with  $\text{C}^+$  also create some  $\text{CO}^+$  which forms additional CO by collisions with atomic hydrogen.

Figure 1 also shows that water ice is mixed up, by at least one decade in column density, to  $\log N_{(\text{H})} \approx 22$ , which coincides about with the vertical  $A_V = 1$ -layer. Figure 4 shows the location

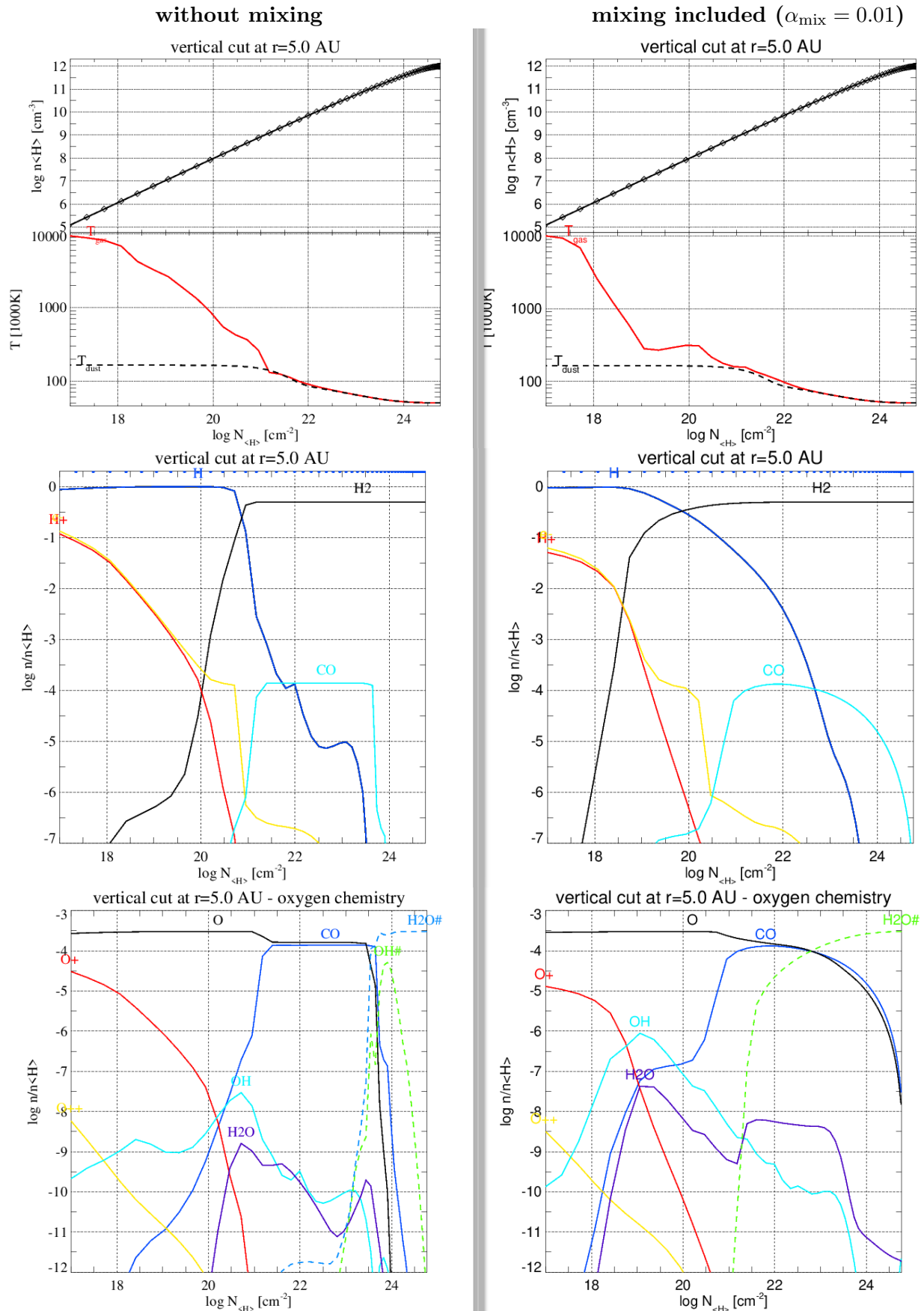


Figure 1: Vertical cuts through our DIANA standard T Tauri model at  $r = 5$  au as function of hydrogen nuclei column density  $N_{\langle H \rangle}$ .

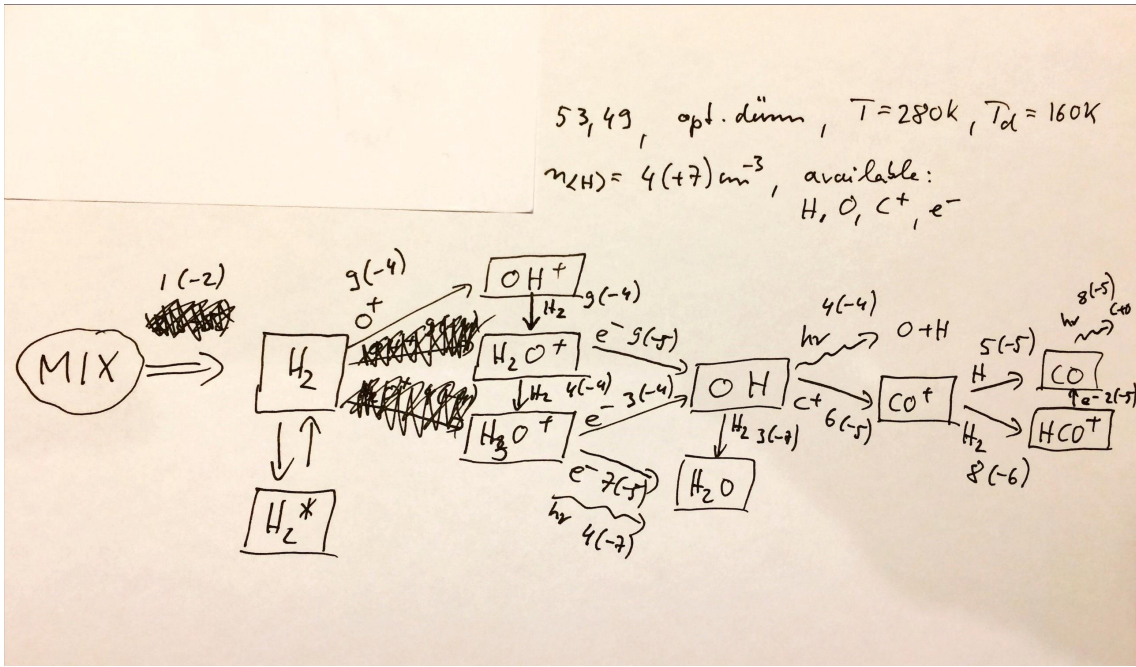


Figure 2: Analysis of the chemical paths leading to OH, H<sub>2</sub>O, and CO formation at  $r=5$  au and about  $\log N_{\langle\text{H}\rangle} [\text{cm}^{-2}] = 19.5$  which is optically thin in both the radial and vertical directions. The numbers “ $X(Y)$ ” are the rates  $X \times 10^Y \text{cm}^{-3}\text{s}^{-1}$ . Everything starts by mixing up H<sub>2</sub>.

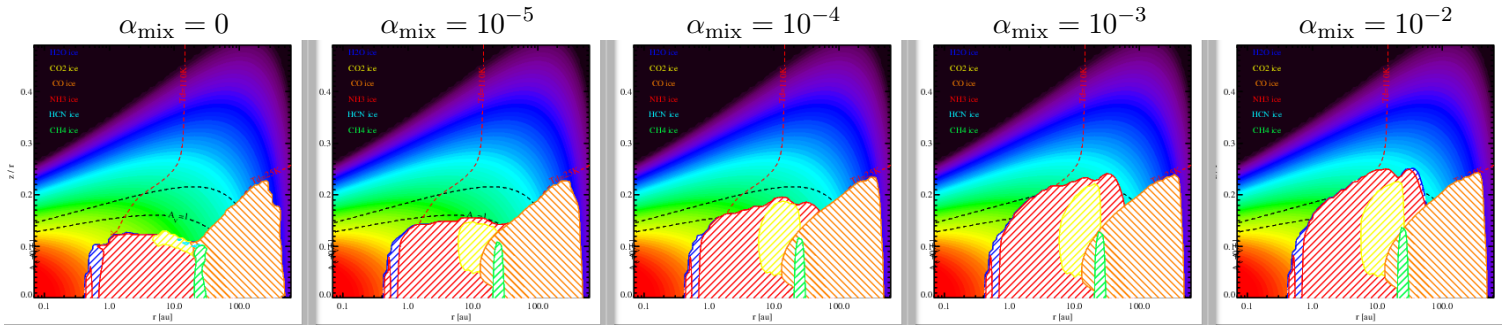


Figure 3: Series of T Tauri standard models with increasing mixing efficiency, showing the location of the ices. The black dashed lines show vertical extinction  $A_V = 0.1$  and  $A_V = 1$ . The red dashed contour line marks  $T_{\text{dust}} = 110\text{K}$ , a classical indicator for the snowline.

of the icy grains in a series of models with increasing  $\alpha_{\text{mix}}$ . This could potentially mean that ice emission features may become visible in the SED. In our standard (non-mixed) models, the ice is located only deep in the midplane of the disc (vertical  $A_V > 10$ ), which does not allow any photons emitted from there to reach the observer. In the mixed models, already for  $\alpha_{\text{mix}} = 10^{-4}$ , we find icy grains above  $A_V = 1$ . The sublimating (photo-desorbing) water ice creates additional cold gas-phase H<sub>2</sub>O on the way up, which creates a second bump of the H<sub>2</sub>O concentration at about  $\log N_{\langle\text{H}\rangle} \approx 21.5 \dots 23$  in Fig. 1.

The gas temperature structure (Fig. 1, upper panel) is also affected. The gas temperature decreases earlier due to increased molecular line cooling in particular by OH. Deeper in the disk, the down-mixing of atomic hydrogen stimulates H<sub>2</sub>-formation with associated heating mechanisms, which results in larger  $T_g - T_d$  contrasts around  $N_{\langle\text{H}\rangle} \approx 10^{22} \text{cm}^{-2}$ .

Bottom line, diffusive eddy-mixing seems to produce a richer mixture of atoms, molecules and ices, which creates a more active chemistry with the typical PDR-like transitions  $\text{H} \rightarrow \text{H}_2$ ,  $\text{O} \rightarrow \text{OH} \rightarrow \text{H}_2\text{O}$ ,  $\text{C}^+ \rightarrow \text{C} \rightarrow \text{CO}$ , and gas  $\rightarrow$  ice occurring already at smaller column densities.

## 5 Further remarks, ideas and outlook

- It would be relatively easy to implement radial diffusion as well.
- In order to accelerate the convergence of the global iterations in PRODIMO, one could implement a new inward-upward sweep of the chemistry that is performed after each outward-downward sweep. This is similar to what [Rimmer & Helling \(2016\)](#) do. Molecular column densities and line optical depths would need to be stored after each outward-downward sweep and then re-used during such an inward-upward sweep. This would give us an opportunity to also have proper column densities from below and line optical depths outside-in and across the disk to improve photochemistry and the line escape probability for heating/cooling.
- At the moment, only the eddy-diffusion is implemented, and all species are assumed to be mixed by the same local diffusion coefficient  $K$ , in which case the element abundances remain constant throughout the disk. However, this is likely to be a quite rough approximation, in particular when we consider a mixture of ice and gas species. The Ice species are transported with the dust grains, and the grains are only moved by the larger turbulent eddies. In order to arrive at an effective dust particle diffusion coefficient, the advective effect of all individual turbulent eddies has to be averaged. This procedure is carried out, with different methods and approximations, by [Dubrulle et al. \(1995\)](#), [Schr apler & Henning \(2004\)](#) and [Youdin & Lithwick \(2007\)](#). The result of [Schr apler & Henning \(2004\)](#), see their Eq. 27), is

$$K_{\text{ice}} = \frac{K}{1 + St} \quad (28)$$

where  $St$  is the Stokes number given by

$$St = \frac{\tau_{\text{stop}}}{\tau_{\text{eddy}}} = \frac{\frac{\rho_d a}{\rho v_{\text{th}}}}{\frac{H}{\alpha_{\text{mix}} c_s}} = \sqrt{\frac{\pi}{8}} \frac{\rho_d a \alpha_{\text{mix}}}{\rho H} \quad (29)$$

where  $a$  is the grain size. Not obvious how to choose  $a$  as we actually need the cumulative effect of all grains of different sizes on the diffusive flux, where it also must be debated how the ice is distributed onto the bare grains of different sizes, and how the size dust distribution is altered by ice formation. The factor  $\sqrt{\pi/8}$  is because  $c_s^2 = kT/\mu$  but  $v_{\text{th}}^2 = 8kT/(\pi\mu)$ .

Assuming that we know  $K$  and  $K_{\text{ice}}$ , and assuming that all vertical element fluxes  $\Phi_k$  must vanish everywhere in the disc in the time-independent, stationary limit, we can derive a local condition for each element  $k$  from Eq. (11)

$$\Phi_k = -K n \frac{\partial}{\partial z} \left( \frac{\sum_{\text{gas}} s_{ik} n_i}{n} \right) - K_{\text{ice}} n \frac{\partial}{\partial z} \left( \frac{\sum_{\text{ice}} s_{ik} n_i}{n} \right) = 0 \quad (30)$$

Defining the element abundances present in the gas and ice, respectively, as

$$\epsilon_k = \epsilon_k^{\text{gas}} + \epsilon_k^{\text{ice}} \quad , \quad n_{\langle \text{H} \rangle} \epsilon_k^{\text{gas}} = \sum_{\text{gas}} s_{ik} n_i \quad , \quad n_{\langle \text{H} \rangle} \epsilon_k^{\text{ice}} = \sum_{\text{ice}} s_{ik} n_i \quad (31)$$

we find

$$\boxed{\frac{\partial}{\partial z} \left( \frac{n_{\langle \text{H} \rangle} \epsilon_k^{\text{gas}}}{n} \right) + \frac{K_{\text{ice}}}{K} \frac{\partial}{\partial z} \left( \frac{n_{\langle \text{H} \rangle} \epsilon_k^{\text{ice}}}{n} \right) = 0} \quad (32)$$

1. **Small Stokes numbers:** In the limiting case of small dust radii  $a$  and/or large gas densities  $\rho$ , we have  $St \ll 1$ , i.e. well-coupled grains, and hence  $K_{\text{ice}} \approx K$ . Thus, from Eq. (32), we obtain

$$\frac{n_{\langle\text{H}\rangle} \epsilon_k}{n} = \text{const} . \quad (33)$$

previously referred to as “the element abundances are constant”. Clearly, when all species are transported in equal ways, and hence mixed with the same efficiency, the element abundances cannot change. However, Eq. (32) actually states a somewhat different result! Diffusion will make sure that, on the long run, the concentration of elements as measured with respect to the total gas particle density  $n$  become constant. At the locations of the major phase transitions  $\text{H}^+ \rightarrow \text{H}$  and  $\text{H} \rightarrow \text{H}_2$ , where the mean molecular mass changes by roughly a factor of 2 each, the element abundances must change as well, in the opposite direction, approximately  $\epsilon_k \propto 1/\mu$ . Otherwise, when  $\mu$  is constant, we have  $n \propto n_{\langle\text{H}\rangle}$  and hence indeed  $\epsilon_k = \text{const}$ . But considering a complete column from ionised down to molecular conditions, Eq. (33) states that the helium abundance, for instance, must be about  $4\times$  larger in the ionised regions as compared to the molecular regions.

2. **Large Stokes numbers: The cold trap:** In the limiting case of large Stokes numbers ( $a \rightarrow \infty$  and/or  $\rho \rightarrow 0$ , we have  $K_{\text{ice}} \ll K$ , and thus from Eq. (32)

$$\frac{n_{\langle\text{H}\rangle} \epsilon_k^{\text{gas}}}{n} = \text{const} . \quad (34)$$

This is a remarkable result. If an element can freeze out anywhere in the column, a rather low level of  $\epsilon_k^{\text{gas}}$  is established there, and this low level of  $\epsilon_k^{\text{gas}}$  is then mapped out all over the column, irrespective of the local  $\epsilon_k^{\text{ice}}$ . This effect is commonly known as a “cold trap”. Since the cold mirror in my bathroom cannot move, but the air does, all the water in the warm air in the room (after taking a shower) will continue to diffuse toward and condense onto that mirror, until eventually the supersaturation of the air over the mirror approaches unity. If the mirror temperature is kept lower than air temperature, this will eventually cause under-saturation of water in the warm gas in the room.

To order to implement Eq. (32) in PRODIMO, let us define the ice ratio by  $X_k = \epsilon_k^{\text{ice}}/\epsilon_k$ :

$$\begin{aligned} \frac{\partial}{\partial z} \left( \frac{n_{\langle\text{H}\rangle} (1 - X_k) \epsilon_k}{n} \right) + \frac{K_{\text{ice}}}{K} \frac{\partial}{\partial z} \left( \frac{n_{\langle\text{H}\rangle} X_k \epsilon_k}{n} \right) &= 0 \\ \frac{\partial}{\partial z} \left( \frac{n_{\langle\text{H}\rangle} \epsilon_k}{n} \right) (1 - X_k) - \frac{n_{\langle\text{H}\rangle} \epsilon_k}{n} \frac{\partial X_k}{\partial z} + \frac{K_{\text{ice}}}{K} \left( \frac{\partial}{\partial z} \left( \frac{n_{\langle\text{H}\rangle} \epsilon_k}{n} \right) X_k + \frac{n_{\langle\text{H}\rangle} \epsilon_k}{n} \frac{\partial X_k}{\partial z} \right) &= 0 \\ \Rightarrow \frac{\partial}{\partial z} \left( \frac{n_{\langle\text{H}\rangle} \epsilon_k}{n} \right) \left( 1 - X_k \left( 1 - \frac{K_{\text{ice}}}{K} \right) \right) - \frac{n_{\langle\text{H}\rangle} \epsilon_k}{n} \frac{\partial X_k}{\partial z} \left( 1 - \frac{K_{\text{ice}}}{K} \right) &= 0 \\ \frac{\partial}{\partial z} \ln \left( \frac{n_{\langle\text{H}\rangle} \epsilon_k}{n} \right) = \frac{\partial X_k}{\partial z} \frac{1 - \frac{K_{\text{ice}}}{K}}{1 - X_k \left( 1 - \frac{K_{\text{ice}}}{K} \right)} & \quad (35) \end{aligned}$$

Equation (35) can be used, in an iterative way, to numerically adjust  $\epsilon_k$  in each column, step by step, from bottom to top

$$\ln \left( \frac{n_{\langle\text{H}\rangle}^{j+1} \epsilon_k^{j+1}}{n^{j+1}} \right) - \ln \left( \frac{n_{\langle\text{H}\rangle}^j \epsilon_k^j}{n^j} \right) = \left( X_k^{j+1} - X_k^j \right) \frac{1 - \frac{K_{\text{ice},j+1/2}}{K^{j+1/2}}}{1 - X_k^{j+1/2} \left( 1 - \frac{K_{\text{ice}}^{j+1/2}}{K^{j+1/2}} \right)} \quad (36)$$

where the notation means  $x^{j+1/2} = \frac{1}{2}(x^j + x^{j+1})$ . The element abundance iterations are then carried out in each column, from bottom to top, where for each step  $j \rightarrow j+1$  we assume that all quantities are fixed (given by the previous results of the chemistry), except for  $\epsilon_k^{j+1}$ .

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