

Modelling and interpreting the isotopic composition of water vapour in convective updrafts: Supplementary material

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1 Ventilation coefficients, Lewis number

The diffusional growth of a cloud particle (droplet or crystal) falling in the ambient air is influenced by its relative motion. The air flow around a particle depends on particle geometry and the Reynolds number. In all cases, the local gradients of heat and vapour are increased around the moving particle, and the diffusional growth rate and latent heat release rate are enhanced over their corresponding values at rest. The effect is measured by the ventilation coefficients for vapour and heat diffusion:

$$f_v = \frac{(dm/dt)}{(dm/dt)_0},$$

$$f_h = \frac{(dQ/dt)}{(dQ/dt)_0},$$

where the subscript 0 refers to the situation when the particle is stationary relative to the air.

Boundary layer theory predicts that f_v and f_h should be proportional to $X_v = Sc^{\frac{1}{3}} Re^{\frac{1}{2}}$ and $X_h = Pr^{\frac{1}{3}} Re^{\frac{1}{2}}$, where $Sc = \mu/\rho K_v$, $Pr = c_p \mu/k_h$ and $Re = \rho U_\infty D/\mu$ are, respectively, the Schmidt, Prandtl and Reynolds numbers and μ is the dynamic viscosity. The functional dependency of f_v on X_v is the same as that of f_h on X_h since the underlying mathematical framework is the same. A Schmidt number for heavy isotopologue can be defined as $Sc' = \eta/\rho K'_v$,

From wind tunnel experiments of evaporating drops, (Beard and Pruppacher, 1971) provide the following expressions for f_v :

$$f_v = \begin{cases} 1 + 0.108 X_v^2 & \text{for } X_v \leq 1.4, \\ 0.78 + 0.308 X_v & \text{for } X_v > 1.4. \end{cases}$$

For ice crystals, we use Pitter et al. (1974) numerical solutions for oblate spheroids (\sim hexagonal plates):

$$f_v = \begin{cases} 1 + 0.142 X_v^2 + 0.054 X_v^4 \ln(0.893 X_v^2) & \text{for } X_v \leq 0.71, \\ 0.937 + 0.178 X_v & \text{for } X_v > 0.71. \end{cases}$$

The calculation of Re for falling drops and droplets is made after Beard (1976) which distinguishes three regimes according to the diameter of the particles. For ice crystals, assumed to be hexagonal plates, we use the procedure given by Heymsfield and Westbrook (2010).

Some computed values of f_v/f_h and f_v/f'_v are compiled in Tables 1 and 2, as a function of particle diameter (the maximum projected length for an hexagonal plate) and altitude within the cloud. As expected from the dependency of f on Re, it is seen that ventilation effects mostly increase with size. f_v/f_h and f_v/f'_v remain, however, close to unity and this justifies the approximation made in this study.

If cloud liquid water and cloud ice behave as pure airborne particles (static relative to the air parcel), then it is obvious that ventilation effects do not matter for fractionation. In particular, cloud droplets whose isotopic content re-equilibrate with that of vapour are small enough to yield values of f_v/f_h and f_v/f'_v that differ from 1 by less than 0.1%. Moreover, it can be easily checked (not shown), that absolute values of f_v and f'_v at such sizes are sufficiently close to 1 to leave the value of τ_{drop} unaltered, such that the criterion for re-equilibrating droplets is unaffected by ventilation.

Ventilation effects are expected to be more important when precipitating particles are considered. Although our study focuses on droplets, let us consider the case of a falling drop for the sake of comparison. In this case the ratio f_v/f'_v differs from 1 by less than 0.7% but f_v/f_h may reach about 0.96. Variations of f_v/f_h produce variations of the coefficient A_l which are limited to 2.5%. Finally, the extent to which f_v/f_h and f_v/f'_v modify α_{kl} is respectively 0.006% and 0.015%

only. By comparison, the relative difference between α_l and α_{kl} is 0.3%. It is clear that ventilation leaves fractionation factors virtually unaffected, even if actual growth rates and latent heat release rates are enhanced by a factor of 8 in our previous computations.

The above results are largely a consequence of K_v/K'_v and $Le = Re/Pr = K_h/K'_v$ being close to unity. If we had $Le = 1$, then we could rigorously set $f_h = f_v$ (the non-dimensional fields of temperature and vapour density around the particle would exactly coincide). The fact that $Le \sim 1$ for a vapour-air mixture is to some extent fortuitous. The kinetic theory of gas for rigid elastic spherical molecules (Chapman and Cowling, 1970) can be used to derive the following approximate expression for the Lewis number:

$$Le = \frac{1}{12} \left(21 \frac{c_p}{c_v} - 5 \right) \frac{25}{68} \sqrt{2} \left(1 + \frac{\Gamma_{\text{H}_2\text{O}}}{\Gamma_{\text{air}}} \right)^2 \times \left(1 + \frac{m_{\text{air}}}{m_{\text{H}_2\text{O}}} \right)^{-\frac{1}{2}}, \quad (1)$$

where $\Gamma_{\text{H}_2\text{O}}$, Γ_{air} , m_{air} and $m_{\text{H}_2\text{O}}$ are respectively collisional diameters and molecular masses of water and air molecules. In deriving the above expression, we have neglected the contribution of vapour to thermal conductivity, and used a modified Eucken factor $\frac{1}{12} \left(21 \frac{c_p}{c_v} - 5 \right)$ as suitable for weakly polar diatomic gases. Taking $\Gamma_{\text{H}_2\text{O}} = 2.65 \times 10^{-8}$ cm (Hirschfelder et al., 1967), $\Gamma_{\text{air}} = 3.6 \times 10^{-8}$ cm (Glassman and Hariis, 1952), $m_{\text{air}}/m_{\text{H}_2\text{O}} = 29/18$, we find $Le \sim 0.8$. A direct calculation (from the expressions of K_v and k_h given in appendix C of the main text) yields 0.87. It is clear that $Le \sim 1$ is a result of the particular ratios of collisional diameters and molecular masses for water and air, and it is not obvious that this result can be transposed to other gases mixtures (such as in the problem of sulphuric acid deposition for instance).

2 Thermal relaxation time and freezing time

The characteristic time of freezing t_f is computed for droplets freely falling in air. We follow the approach of Johnson and Hallett (1968) and briefly summarize their argument here.

Consider a droplet initially supercooled to the temperature of its surrounding environment $T^{(\infty)}$. The initial stage of freezing corresponds to the very fast growth of ice dendrites within the supercooled droplet, until the release of latent heat inside the droplet increases its temperature up to the freezing equilibrium value $T^{(\text{eq})} = 0^\circ\text{C}$. This stage is assumed to happen instantly, and turns the droplet into a mixture of liquid water and ice, with a liquid fraction $1 - c_l (T^{(\text{eq})} - T^{(\infty)}) / L_i$.

A spherical shell of ice then appears from the surface of the droplet and thickens as the freezing front propagates inward. The rate of freezing at this stage depends on the rate

of heat transfer to the environment, by heat conduction and evaporation to environmental air. The ice water (inner) interface where freezing happens is assumed at radial distance r from the centre of the droplet and at $T^{(\text{eq})} = 0^\circ\text{C}$. The ice air (outer) interface is at radial distance a (initial radius) and its temperature $T^{(s)}$ is not much below $T^{(\text{eq})} = 0^\circ\text{C}$. Hence, ice evaporation should occur at the freezing droplet surface even when the environment is ice supersaturated at temperature $T^{(\infty)}$.

Then, the rate of release of latent heat by freezing is equal to the rate of heat conduction through the ice shell, itself equal to the rate of heat loss by conduction and evaporation to environmental air. These conditions yields (Mason, 1956, Eq.(1)):

$$-L_f \rho_l r^2 \frac{dr}{dt} \left(1 - c_l \frac{T^{(\text{eq})} - T^{(\infty)}}{L_f} \right) = -k_i a r \frac{T^{(s)} - T^{(\text{eq})}}{a - r}, \quad (2)$$

$$-k_i a r \frac{T^{(s)} - T^{(\text{eq})}}{a - r} = a k_h f_h \left(T^{(s)} - T^{(\infty)} \right) + L_i 4\pi a K_v f_v \left(\rho^{(s)} - \rho^{(\infty)} \right), \quad (3)$$

where k_i is the heat conductivity of ice, L_f is the latent heat of fusion, ρ_l is the density of liquid water and c_l is its heat capacity.

For the sake of simplicity, we assume that the environment is saturated over ice, and we set ventilation coefficients f_h and f_v to unity (droplets of negligible fall velocity). Then, using Eq. (A4) of the main text and eliminating $T^{(s)}$ between Eqs. (2) and (3) yields:

$$\frac{a^2 \rho_l L_f \left(1 - c_l \frac{T^{(\text{eq})} - T^{(\infty)}}{L_f} \right) dy}{k'_{h|i} (T^{(\text{eq})} - T^{(\infty)})} \frac{dy}{dt} = - \frac{1}{(1-m)y^2 + my} \quad (4)$$

where $y = r/a$, $k'_{h|i} = \left(k_h + \frac{L_i K_v}{T^{(\infty)}} \left(\frac{L_i}{R_v^* T^{(\infty)}} - 1 \right) \rho_{\text{sat}}^i \right)$ and $m = k'_{h|i} / k_i$.

Integrating Eq. (4) from $(t=0, y=1)$ to $(t=t_f, y=0)$ yields the expression for the freezing time t_f :

$$t_f = \frac{a^2 \rho_l L_f \left(1 - c_l \frac{T^{(\text{eq})} - T^{(\infty)}}{L_f} \right)}{3k'_{h|i} (T^{(\text{eq})} - T^{(\infty)})} \left(1 + \frac{m}{2} \right). \quad (5)$$

As Johnson and Hallett (1968) note, $m \ll 1$ in air. Thus, Eq. (5) finally yields:

$$t_f = \frac{a^2 \rho_l L_f \left(1 - c_l \frac{T^{(\text{eq})} - T^{(\infty)}}{L_f} \right)}{3k'_{h|i} (T^{(\text{eq})} - T^{(\infty)})}. \quad (6)$$

This corresponds to Eq. (5) of Johnson and Hallett (1968) and has been cross-checked against observations in the same

work. Freezing time is thus governed by the rate of extraction of latent heat by conduction and evaporation to environmental air while heat conduction through the ice phase occurs over a negligible time (hence $m \ll 1$).

t_f is infinite in the limit $T \rightarrow 0^\circ\text{C}$. However, at small supercoolings ($T^{(\text{eq})} - T$), other mechanisms extract heat more efficiently than conduction and evaporation to air. Namely, in the vicinity of the 0°C level, droplets freeze to a large extent by contact with precipitating ice crystals, in which case latent heat extraction happens very fast by conduction through ice. Thus, Eq. (6) must be considered as a lower bound on the freezing relaxation time, and used to show, when it is smaller than the isotopic relaxation time, that freezing does not lead to isotopic fractionation.

The definition of thermal relaxation time t_h is provided by Mason (1956) assuming for simplicity a spherical droplet or ice crystal freely suspended in the environmental air at temperature $T^{(\infty)}$. The ventilation factors are again set to unity (negligible fall velocity). The droplet or crystal temperature is further assumed to have homogeneous temperature T . Then, the enthalpy of the droplet or crystal may change as a result of heat conduction to air and evaporation or condensation. This enthalpy budget yields, using Eq. (A4) of the main text in the same way as above:

$$\frac{4}{3}\pi a^3 \rho_{l,i} c_{l,i} \frac{dT}{dt} = -4\pi a k'_{h|l,i} (T^{(\infty)} - T), \quad (7)$$

where $k'_{h|l}$ is defined as $k'_{h|i}$ but for liquid L_l and ρ_{sat}^l .

The thermal relaxation time for droplets or ice crystals t_h immediately follows:

$$t_h = \frac{\rho_{l,i} c_{l,i} a^2}{3k'_{h|l,i}}. \quad (8)$$

One notices from Eq. (8) that t_h is smaller for ice crystals than for droplets. The fact that thermal relaxation times are much smaller than isotopic relaxation times means that it is safe to derive the evolution of isotopic ratios by assuming steady-state solutions of heat transfer equations as we did in Appendix B of the main text.

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alt. [km]	f_v/f_h							
	diameter	10 μm	30 μm	50 μm	100 μm	200 μm	400 μm	800 μm
2	drop	0.99999	0.99964	0.99841	0.98989	0.97621	0.96752	0.96127
	crystal							
6	drop	0.99999	0.99975	0.99889	0.99257	0.97892	0.97044	0.96418
	crystal	0.99999	0.99987	0.99959	0.99818	0.99324	0.9879	0.98124
10	drop	0.99999	0.99983	0.99923	0.99467	0.99643	0.97414	0.96818
	crystal	0.99999	0.99991	0.99972	0.99871	0.9945	0.98994	0.98403
14	drop							
	crystal	1	0.99994	0.99981	0.9991	0.99585	0.99231	0.98759

Table 1. Tabulated values of f_v/f_h as a function of particle diameter and altitude within the cloud.

alt. [km]	f_v/f'_v							
		10 μm	30 μm	50 μm	100 μm	200 μm	400 μm	800 μm
2	drop	1	0.99994	0.99974	0.99834	0.99597	0.99445	0.99335
	crystal	1						
6	drop	1	0.99996	0.99981	0.9987	0.99621	0.99465	0.99348
	crystal	1	0.99998	0.99993	0.99968	0.9988	0.99784	0.99664
10	drop	1	0.99997	0.99985	0.99897	0.99643	0.99483	0.99361
	crystal	1	0.99998	0.99995	0.99975	0.99892	0.99801	0.99683
14	drop	1						
	crystal	1	0.99999	0.99995	0.99978	0.99899	0.99812	0.99696

Table 2. Tabulated values of f_v/f'_v (for the HDO/H₂O system) as a function of particle diameter and altitude within the cloud.