Dynamics II: Oxygen Isotopes, 2. July 2007

1. Derive an expression for the temperature dependence of δ_c in a Rayleigh system. First calculate
$$\frac{d\ln(\delta_c+1)}{dT} = \frac{d}{dT}\cdots$$
using the equilibrium condition $\delta_{v0} = 1/\alpha_0 - 1$.

2. Plot $\delta^{18}O_v$ and $\delta^{18}O_l$ for an open and closed system, depending on f. Remember, f, the remaining water in the vapour phase, depends on the condensation temperature. Assume $T_0 = 20°$C i.e. $f = 1.0$ at $T = T_0$, lower condensation temperatures lead to lower f with $0.0 < f < 1.0$. Further assume
$$\overline{\alpha} = 1/2\,(\alpha(20°C) + \alpha(T_c)).$$
Where are the largest differences between the open and closed system?

3. The north wind advects dry air (h=50%, $\|v\| = 15\,ms^{-1}$, $T_0 = 20°$C) over the Mediterranean. Calculate the corresponding deuterium excess and the δ of the precipitation ($T_c = 15°$C, assume Rayleigh fractionation). Increase h, v, and T by 20 percent (3 separate calculations). What is the effect on δ_c ?

Definition of Delta-values:
$$\delta_A = \left(\frac{R_A}{R_{VSMOW}} - 1\right) \text{ where } R_A = [^{18}O]/[^{16}O], \text{ or } [D]/[^1H].$$
Absolute values for VSMOW:
$$^{18}O: \quad R_{VSMOW} = (2005.2 \pm 0.45)\cdot 10^{-6} \quad (1)$$
$$D: \quad R_{VSMOW} = (155.76 \pm 0.05)\cdot 10^{-6} \quad (2)$$
Usually, δ-values are given in ‰:
$$\delta_A = \left(\frac{R_A}{R_{VSMOW}} - 1\right)\cdot 1000 \quad (3)$$
"permill" is not a physical unit!

Consider (water) phase change between A and B (e.g. liquid and vapour): $R_A = \alpha_{A-B}R_B$, where R_A,R_B isotopic (water) compositions in phase A and B, α_{A-B} the *fractionation factor*. Empirical α values for Liquid → Vapour, and Ice → Vapour:
$$^{18}O: \quad ln\alpha_{L-V} = \frac{1.137}{T^2}\cdot 10^3 - \frac{0.4156}{T} - 2.0667\cdot 10^{-3} \quad (4)$$
$$^{18}O: \quad ln\alpha_{I-V} = \frac{11.839}{T} - 28.224\cdot 10^{-3} \quad (5)$$
$$D: \quad \ln\alpha_{L-V} = \frac{24.844}{T^2}\cdot 10^3 - \frac{76.248}{T} + 52.612\cdot 10^{-3} \quad (6)$$
$$D: \quad \ln\alpha_{I-V} = \frac{16.288}{T^2} - 93.4\cdot 10^{-3} \quad (7)$$

$$\frac{dc_i}{dc} = \alpha(T)\frac{v_i}{v} \quad \text{with } dc_i = -dv_i \text{ and } dc = -dv \tag{8}$$

$$\frac{dv_i}{v_i} = \alpha(T)\frac{dv}{v} \quad \text{integrate from time 0 to t} \tag{9}$$

$$\ln v_i|_0^t = \overline{\alpha}\ln v|_0^t \quad \text{where } \overline{\alpha} \text{ is a value } \in [0,t] \tag{10}$$

$$\frac{v_i(t)}{v_i(0)} = \left(\frac{v(t)}{v(0)}\right)^{\overline{\alpha}} \quad \text{with } R_v = \frac{v_i}{v} \text{ and } f = \frac{v(t)}{v(0)} \tag{11}$$

$$R_v(t) = R_v(0)f^{\overline{\alpha}-1} \tag{12}$$

With liquid condensate c, vapour v, c_i and v_i corresponding isotope fraction, and $(1-f)$ rainout fraction.

$$\delta_v = [(\delta_{v_0}+1)f^{\overline{\alpha}-1}-1] \tag{13}$$

$$\delta_c = [\alpha(\delta_{v_0}+1)f^{\overline{\alpha}-1}-1] \tag{14}$$

$$R_c(t) = \frac{c_i(t)}{c(t)} = \alpha\frac{v_i(t)}{v(t)} = \alpha R_v(t) \tag{15}$$

$$c_i(t)+v_i(t) = v_{i_0} \quad \text{and} \quad c(t)+v(t) = v_0 \tag{16}$$

$$\frac{c_i(t)}{c(t)} = \frac{v_{i_0}-v_i(t)}{v_0-v(t)} \quad \text{with } c(t) = v_0(1-f) \text{ and } v(t) = v_0 f \tag{17}$$

$$= \frac{v_{i_0}}{v_0}\frac{1}{1-f} - \frac{v_i(t)}{v(t)}\frac{1}{f^{-1}-1} \tag{18}$$

$$\delta_v = (\delta_{v0}+1)\frac{1}{\alpha}\left[\frac{1}{(\frac{1}{\alpha}-1)f+1}\right]-1 \tag{19}$$

$$\delta_c = (\delta_{v0}+1)\left[\frac{1}{(\frac{1}{\alpha}-1)f+1}\right]-1 \tag{20}$$

Definition GMWL: δD= 8 $\times\delta^{18}$O + 10‰
Definition deuterium excess: d =δD − 8 $\times\delta^{18}$O

$$\frac{D_{H_2^{18}O}}{D_{H_2^{16}O}} = 0.9723 \tag{21}$$

$$\frac{D_{^1HD^{16}O}}{D_{H_2^{16}O}} = 0.9755 \tag{22}$$

$$1 + {}^{2,18}\delta = (1-k)\frac{\frac{1}{\alpha}-h(1 + {}^{2,18}\delta_0)}{1 - h} \tag{23}$$

$$k = \begin{cases} 0.006 & :^{18}O \\ 0.00528 & :D \end{cases} \quad \|v_h\| < 7m/s \tag{24}$$

$$k = \begin{cases} 2.85\cdot 10^{-5}+8.2\cdot 10^{-5}\cdot\|v_h\| & :^{18}O \\ 2.508\cdot 10^{-5}+7.216\cdot 10^{-5}\cdot\|v_h\| & :D \end{cases} \quad \|v_h\| > 7m/s \tag{25}$$