Diffusion of water vapor onto a cloud droplet

Growth of cloud droplet by diffusion involves two simultaneous processes.
1. Water vapor diffuses onto the condensation nucleus/droplet
2. Heat released by the latent heat release diffuses outward from the cloud droplet

From Fick's second law

$$\frac{\partial n}{\partial t} = D_v \nabla^2 n \tag{1}$$

Assume steady state

$$\frac{\partial n}{\partial t} = 0 = D_v \nabla^2 n \tag{2}$$

In spherical coordinates and assuming, by symmetry, only radial dependence (no angular dependence)

$$\nabla^2 n = \frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d}{dr}n\right) = 0 \tag{3}$$

$$\left(r^2\frac{d}{dr}n\right) = C_1 \tag{4}$$

$$\frac{d}{dr}n = \frac{C_1}{r^2} \tag{5}$$

$$\int dn = \int \frac{C_1}{r^2}dr \tag{6}$$

$$\left[n(\infty) - n(r)\right] = -C_1\left[0 - \frac{1}{r}\right] = \frac{C_1}{r}$$

$$n(r) = n(\infty) - \frac{C_1}{r} \tag{7}$$

We have the further constraint that at r_{drop}, $n = n_r$ such that

$$n(r_{drop}) = n(\infty) - \frac{C_1}{r_{drop}}$$

$$C_1 = \left[n(\infty) - n(r_{drop})\right]r_{drop} \tag{8}$$

such that

$$n(r) = n(\infty) - \frac{r_{drop}}{r}\left[n(\infty) - n(r_{drop})\right] \tag{9}$$

The flux is

$$F_n = -D_v\frac{dn}{dr} = -D_v\frac{r_{drop}}{r^2}\left[n(\infty) - n(r_{drop})\right]$$

$$F_n(r) = -\frac{D_v}{r}\frac{r_{drop}}{r}\left[n(\infty) - n(r_{drop})\right] = -\frac{D_v}{r}\left[n(\infty) - n(r)\right] \tag{10}$$

The total flux at the drop surface where $r = r_{drop}$ is the flux (density) times the area of the drop:

$$F_{n,r_{drop}}A_{drop} = -\frac{D_v}{r_{drop}}\left[n(\infty) - n(r_{drop})\right]4\pi r_{drop}^2 = -D_v\left[n(\infty) - n(r_{drop})\right]4\pi r_{drop} \tag{11}$$

The change in the mass of the droplet is this number density flux times the mass per molecule

$$\frac{dm_{drop}}{dt} = D_v\left[n(\infty) - n(r_{drop})\right]4\pi r_{drop}m_v = D_v\left[\rho_v(\infty) - \rho_v(r_{drop})\right]4\pi r_{drop} \tag{12}$$

where m_v is the mass per molecule or per mole depending on the units of n. Clearly, for the droplet to grow, the environmental number density of water molecules, $n(\infty)$, must exceed that of the number density at the surface of the droplet, $n(r_{drop})$. If on the other hand $n(r_{drop})$ is greater than $n(\infty)$, then the cloud droplet will evaporate.

The latent heat release from the condensation of the water vapor causes the droplet to warm above the ambient temperature and this extra sensible heat diffuses away from the droplet.

$$\frac{dQ}{dt} = 4\pi r K_s\left[T(r) - T(\infty)\right] \tag{13}$$

where K_s ($= \rho\, C_p\, D_s$) is the thermal conductivity of the air in units of kg/m^3 J/kg/K m^2/s = J/m/s/K.

The change in the temperature of the droplet is

$$\frac{4}{3}\pi r^3 \rho_L C_L \frac{dT_r}{dt} = L\frac{dm}{dt} - \frac{dQ}{dt} \tag{14}$$

If we assume steady state droplet temperature, then

$$L\frac{dm}{dt} = \frac{dQ}{dt} = LD_v\left[\rho_v(\infty) - \rho_v(r_{drop})\right]4\pi r_{drop} = 4\pi r_{drop}K\left[T(r_{drop}) - T(\infty)\right] \tag{15}$$

$$\frac{\left[\rho_v(\infty) - \rho_v(r_{drop})\right]}{\left[T(r_{drop}) - T(\infty)\right]} = \frac{K}{LD_v} \tag{16}$$

The water vapor density over the droplet surface is the determined by the saturation vapor pressure over a curved surface such that

$$\rho_{vr_{drop}} = \frac{e_s'(r, T_{r_{drop}})}{R_v T_{r_{drop}}} = \frac{e_s(r = \infty, T_{r_{drop}})}{R_v T_{r_{drop}}}\left[1 - \frac{b}{r_{drop}^3}\right]\exp\left(\frac{a}{r_{drop}}\right) \tag{17}$$

Equations (16) and (17) can be solved simultaneously numerically to determine T_{drop}, ρ_{vdrop} and r_{drop} versus time. There is an alternative solution shown below.

Growth of the droplet size: Alternative approximate solution by Mason (1971)

The saturation vapor pressure is related to the water vapor density via the ideal gas law

$$e_s = \rho_{vs} R_v T$$

$$\rho_{vs} = \frac{e_s}{R_v T} \tag{18}$$

The logarithmic derivative is given as

$$\frac{d\rho_{vs}}{\rho_{vs}} = \frac{de_s}{e_s} - \frac{dT}{T} = \frac{L}{R_v}\frac{dT}{T^2} - \frac{dT}{T} \tag{19}$$

where we have used the Clausius Clapeyron equation (so this equation does NOT involve the droplet surface curvature effects). Integrating (19) from T_{drop} to T and assuming $T/T_{drop} \sim 1$ yields

$$\int_{T_{drop}}^{T} \frac{d\rho_{vs}}{\rho_{vs}} = \ln(\rho_{vs})\Big|_{T_{drop}}^{T} = \int_{T_{drop}}^{T} \left(\frac{L}{R_v}\frac{dT}{T^2} - \frac{dT}{T} \right) = -\frac{L}{R_v}\frac{1}{T}\Big|_{T_{drop}}^{T} - \ln(T)\Big|_{T_{drop}}^{T}$$

$$\ln\left(\frac{\rho_{vs}[T]}{\rho_{vs}[T_{drop}]} \right) = -\frac{L}{R_v}\left(\frac{1}{T} - \frac{1}{T_{drop}} \right) - \ln\left(\frac{T}{T_{drop}} \right)$$

$$\ln\left(\frac{\rho_{vs}[T]}{\rho_{vs}[T_{drop}]} \right) = \frac{L}{R_v}\left(\frac{T - T_{drop}}{T_{drop}T} \right) - \ln\left(1 + \frac{T - T_{drop}}{T_{drop}} \right)$$

$$\ln\left(\frac{\rho_{vs}[T]}{\rho_{vs}[T_{drop}]} \right) = \frac{L}{R_v}\left(\frac{T - T_{drop}}{T_{drop}T} \right) - \left(\frac{T - T_{drop}}{T_{drop}} \right)$$

$$\ln\left(\frac{\rho_{vs\_env}}{\rho_{vs\_drop}} \right) = \left(T_{env} - T_{drop} \right)\left(\frac{L}{R_v T_{drop} T_{env}} - \frac{1}{T_{drop}} \right) \tag{20}$$

$$\left(\frac{\rho_{vs\_env} - \rho_{vs\_drop}}{\rho_{vs\_drop}} \right) = \frac{\left(T_{env} - T_{drop} \right)}{T_{env}}\left(\frac{L}{R_v T_{env}} - 1 \right) \tag{21}$$

Subbing from (13) and then (15)

$$\left(\frac{\rho_{vs\_env} - \rho_{vs\_drop}}{\rho_{vs\_drop}} \right) = \left(1 - \frac{L}{R_v T_{env}} \right)\frac{1}{4\pi r K_s T_{env}}\frac{dQ}{dt} = \left(1 - \frac{L}{R_v T_{env}} \right)\frac{L}{4\pi r K_s T_{env}}\frac{dm_{drop}}{dt} \tag{22}$$

(22) shows the fractional difference between saturation vapor densities of the environment minus that at the droplet **_for flat surfaces_**. Note that (22) would actually cause the droplet to evaporate because $T_{env} < T_{drop}$.

We also have (12) that includes the **actual** vapor pressure of the environment which is supersaturated and the actual saturation vapor density over the curved droplet surface. From (12), we can write

$$\frac{\left[\rho_{v\_env}(\infty) - \rho_v(r_{drop})\right]}{\rho_v(r_{drop})} = \frac{1}{D_v 4\pi r_{drop}\rho_v(r_{drop})}\frac{dm_{drop}}{dt} \tag{23}$$

This should be rewritten to include the curvature and solution effects on the droplet surface which means its saturation vapor pressure depends on the size of the droplet according to (9) from the droplet activation notes.

$$\frac{e_s'(r,T)}{e_s(r=\infty,T)} = \frac{\rho_{vs}'(r,T)}{\rho_{vs}(r=\infty,T)} = \left[1 - \frac{b}{r^3}\right]\exp\left(\frac{2\sigma}{rR_v\rho_L T}\right) = \left[1 - \frac{b}{r^3}\right]\exp\left(\frac{a}{r}\right) \tag{24}$$

Therefore (23) can be rewritten as

$$\frac{\left[\rho_{v\_env}(\infty) - \rho_{v\_drop}(r_\infty)\left[1 - \frac{b}{r^3}\right]\exp\left(\frac{a}{r}\right)\right]}{\rho_{v\_drop}(r_\infty)\left[1 - \frac{b}{r^3}\right]\exp\left(\frac{a}{r}\right)} = \frac{1}{D_v 4\pi r_{drop}\rho_v(r_{drop})}\frac{dm_{drop}}{dt}$$

$$\frac{\left[\rho_{v\_env}(\infty)\left[1 + \frac{b}{r^3}\right]\exp\left(-\frac{a}{r}\right) - \rho_{v\_drop}(r_\infty)\right]}{\rho_{v\_drop}(r_\infty)} = \frac{1}{D_v 4\pi r_{drop}\rho_v(r_{drop})}\frac{dm_{drop}}{dt} \tag{25}$$

$$\frac{\left[\rho_{v\_drop}(\infty)f(r) - \rho_{v\_drop}(r_\infty)\right]}{\rho_{v\_drop}(r_\infty)} = \frac{1}{D_v 4\pi r_{drop}\rho_v(r_{drop})}\frac{dm_{drop}}{dt} \tag{26}$$

where
$$f(r) = \left[1 + \frac{b}{r^3}\right]\exp\left(-\frac{a}{r}\right) \cong \left[1 - \frac{a}{r} + \frac{b}{r^3}\right] \tag{27}$$

Subtracting (22) from (26) and assuming $\rho_{v\_drop}(r_\infty) = \rho_{vs\_drop}$,

$$\frac{\left[\rho_{v\_env}(\infty)f(r) - \rho_{vs\_env}\right]}{\rho_{vs\_drop}} = \left[\frac{1}{D_v 4\pi r_{drop}\rho_{vs\_drop}} - \left(1 - \frac{L}{R_v T}\right)\frac{L}{4\pi r K_s T}\right]\frac{dm_{drop}}{dt} \tag{28}$$

$$\frac{\left[\rho_{v\_env}(\infty)f(r) - \rho_{vs\_env}\right]}{\rho_{vs\_drop}} = \left[\frac{1}{D_v 4\pi r_{drop}\rho_{vs\_drop}} - \left(1 - \frac{L}{R_v T}\right)\frac{L}{4\pi r K_s T}\right]\rho_L 4\pi r_{drop}^2\frac{dr_{drop}}{dt} \tag{29}$$

Now we must rearrange (29) to solve for dr_{drop}/dt. So more algebra…

$$\frac{\left[\rho_{v\_env}(\infty)f(r) - \rho_{vs\_env}\right]}{\rho_{vs\_drop}} = \left[\frac{1}{D_v\rho_{vs\_drop}} - \left(1 - \frac{L}{R_v T}\right)\frac{L}{K_s T}\right]\rho_L r_{drop}\frac{dr_{drop}}{dt}$$

$$\frac{\left[\rho_{v\_env}(\infty)f(r) - \rho_{vs\_env}\right]}{\rho_{vs\_drop}} = \left[\frac{\rho_L R_v T}{D_v e_s(r_{drop})} - \left(1 - \frac{L}{R_v T}\right)\frac{\rho_L L}{K_s T}\right]r_{drop}\frac{dr_{drop}}{dt}$$

$$r_{drop}\frac{dr_{drop}}{dt} = \frac{\left[\rho_{v\_env}(\infty)f(r) - \rho_{vs\_env}\right]}{\rho_{vs\_drop}}\Bigg/\left[\left(\frac{L}{R_vT}-1\right)\frac{\rho_L L}{K_s T} + \left[\frac{\rho_L R_v T}{D_v e_s(r_{drop})}\right]\right] \tag{30}$$

We need to do something with the numerator…

$$r_{drop}\frac{dr_{drop}}{dt} = \frac{\dfrac{\left(\rho_v(\infty)f(r)-\rho_{vs\_env}\right)}{\rho_{vs\_drop}}\dfrac{\rho_{vs\_env}}{\rho_{vs\_env}}}{\left(\dfrac{L}{R_vT}-1\right)\dfrac{\rho_L L}{K_s T}+\left[\dfrac{\rho_L R_v T}{D_v e_s(r_{drop})}\right]} = \frac{\dfrac{\left(\rho_{v\_env}(\infty)f(r)-\rho_{vs\_env}\right)}{\rho_{vs\_env}}\dfrac{\rho_{vs\_env}}{\rho_{vs\_drop}}}{\left(\dfrac{L}{R_vT}-1\right)\dfrac{\rho_L L}{K_s T}+\left[\dfrac{\rho_L R_v T}{D_v e_s(r_{drop})}\right]}$$

Now we substitute the supersaturation, $S = e/e_s = \rho_v/\rho_{vs}$, and get

$$r_{drop}\frac{dr_{drop}}{dt} = \frac{\left(S\,f(r)-1\right)\dfrac{\rho_{vs\_env}}{\rho_{vs\_drop}}}{\left(\dfrac{L}{R_vT}-1\right)\dfrac{\rho_L L}{K_s T}+\left[\dfrac{\rho_L R_v T}{D_v e_s(r_{drop})}\right]} \tag{31}$$

So we now need to consider $\rho_{vs\_env}\Big/\rho_{vs\_drop}$ which is the saturation vapor density in the environment divided by the saturation vapor density at the surface of the droplet. There are two issues. First the curvature of the droplet surface means its saturation vapor pressure depends on the size of the droplet according to (9) from the droplet activation notes.

$$\frac{e_s{}'(r,T)}{e_s(r=\infty,T)} = \left[1-\frac{b}{r^3}\right]\exp\left(\frac{2\sigma}{rR_v\rho_L T}\right) = \left[1-\frac{b}{r^3}\right]\exp\left(\frac{a}{r}\right) \tag{32}$$

Second, the temperature at the droplet is higher than that of the environment so the saturation vapor pressure for a flat surface at the droplet is higher than that of the environment.

$$e_s\left(r=\infty,T_{drop}\right) \cong \left[1+\frac{L\{T_{drop}-T_{env}\}}{R_v T_{drop} T_{env}}\right]e_s\left(r=\infty,T_{env}\right) > e_s\left(r=\infty,T_{env}\right) \tag{33}$$

Combining the last two equations

$$e_s{}'\left(r_{drop},T_{drop}\right) = e_s\left(r_\infty,T_{drop}\right)\left[1-\frac{b}{r^3}\right]\exp\left(\frac{a}{r}\right) \cong e_s\left(r_\infty,T_{env}\right)\left[1+\frac{L\{T_{drop}-T_{env}\}}{R_v T_{drop} T_{env}}\right]\left[1-\frac{b}{r^3}\right]\exp\left(\frac{a}{r}\right) \tag{34}$$

Also we are dealing with water vapor densities rather than vapor pressures so there is an additional conversion required

$$\frac{\rho_{vs\_env}}{\rho_{vs\_drop}} = \frac{e_{vs\_env}}{e_{vs\_drop}}\frac{R_v T_{drop}}{R_v T_{env}} = \frac{e_{vs\_env}}{e_{vs\_drop}}\frac{T_{drop}}{T_{env}} \tag{35}$$

Combining these last two equations yields

$$\frac{\rho_{vs\_env}}{\rho_{vs\_drop}} = \frac{e_{vs\_env}}{e_{vs\_drop}}\frac{T_{drop}}{T_{env}} = \frac{1}{\left[1+\dfrac{L\{T_{drop}-T_{env}\}}{R_v T_{drop} T_{env}}\right]\left[1-\dfrac{b}{r^3}\right]\exp\left(\dfrac{a}{r}\right)}\frac{T_{drop}}{T_{env}} \tag{36}$$

$$\frac{\rho_{vs\_env}}{\rho_{vs\_drop}} = \frac{T_{drop}}{T_{env}}\left[1-\frac{L\{T_{drop}-T_{env}\}}{R_v T_{drop} T_{env}}\right]\left[1+\frac{b}{r^3}\right]\exp\left(-\frac{a}{r}\right) \tag{37}$$

$$\frac{\rho_{vs\_env}}{\rho_{vs\_drop}} = \left[1+\frac{T_{drop}-T_{env}}{T_{env}}-\frac{L\{T_{drop}-T_{env}\}}{R_v T_{drop} T_{env}}-\frac{a}{r}+\frac{b}{r^3}\right] \tag{38}$$

$$\frac{\rho_{vs\_env}}{\rho_{vs\_drop}} = \left[1+\frac{T_{drop}-T_{env}}{T_{env}}\left(1-\frac{L}{R_v T_{drop}}\right)-\frac{a}{r}+\frac{b}{r^3}\right] \tag{39}$$

Now let's try to understand the size of the non-unity terms. From (16) and the definition of K, we can write

$$\left[T(r_{drop})-T(\infty)\right] = \frac{LD_v}{K}\left[\rho_v(\infty)-\rho_v(r_{drop})\right] = \frac{LD_v}{\rho C_p D_s}\left[\rho_v(\infty)-\rho_v(r_{drop})\right] \tag{40}$$

The two diffusivities, the sensible heat, D_s, and diffusion of water vapor in air, D_v, are similar. The diffusion of sensible heat is the result of the diffusion of N_2 and O_2 molecules through other N_2 and O_2 molecules. The diffusion of water vapor is a bit different because it is the diffusion of water vapor molecules through N_2 and O_2 molecules. We can guess that the collisional crosssection is larger for water molecules which will decrease the diffusivity but the mass of water vapor is smaller which will increase the diffusivity. So we can argue crudely that D_s and D_v, are similar so their ratio is about 1. The supersaturation is perhaps a percent of the saturation value. Near the surface, a rough approximation is $\rho_v/\rho_a \sim 1\%$. So $\Delta\rho_v/\rho_a \sim$ 1e-4. $L/C_p \sim$ 2.5e6/1e3 K = 2.5e3 K. So the temperature difference for near surface conditions is of the order of 2.5e3 K 1e-4 = 0.25 K. At colder temperatures, the temperature difference will be still smaller because less water vapor is available in the air and therefore less latent heating to drive a temperature difference. Therefore the T difference term in (39) is approximately

$$\frac{T_{drop}-T_{env}}{T_{env}}\left(-\frac{L}{R_v T_{drop}}\right) \sim -\frac{0.25}{250}20 = -0.02$$

This is comparable to the $-a/r$ term for typical supersaturations. So

$$\frac{\rho_{vs\_env}}{\rho_{vs\_drop}} = \left[1-\Delta\right] \tag{41}$$

where Δ can reach a few percent near the surface and is less at colder temperatures at higher altitudes.

Now we return to the other term in the numerator of (31), $\left(S\,f(r)-1\right)$.

$$\left(S\,f(r)-1\right) = \frac{\rho_v}{\rho_{vs}}\left[1+\frac{b}{r^3}\right]\exp\left(-\frac{a}{r}\right)-1 \cong \frac{\rho_v}{\rho_{vs}}\left[1-\frac{a}{r}+\frac{b}{r^3}\right]-1 \cong S-1-\frac{a}{r}+\frac{b}{r^3} \tag{42}$$

Combining (41) and (42), the numerator of (31) becomes

$$\left(S\, f(r) - 1\right)\frac{\rho_{vs\_env}}{\rho_{vs\_drop}} \cong \left(S - 1 - \frac{a}{r} + \frac{b}{r^3}\right)[1 - \Delta] \cong \left(S - 1 - \frac{a}{r} + \frac{b}{r^3}\right) \tag{43}$$

Plugging (43) into (31) yields when the supersaturations are not too large

$$r_{drop}\frac{dr_{drop}}{dt} = \frac{\left(S - 1 - \dfrac{a}{r} + \dfrac{b}{r^3}\right)}{\left(\dfrac{L}{R_v T} - 1\right)\dfrac{\rho_L L}{K_s T} + \left[\dfrac{\rho_L R_v T}{D_v e_s(r_{drop})}\right]} \tag{44}$$

According to Rogers and Yau, this equation estimates the growth rate of cloud droplets quite accurately.

Cloud droplet growth by diffusion