

# Air Pollution ENV-409

## Multiphase equilibria solutions

There is little  $\text{SO}_4^{2-}$  in the area so the relevant equilibrium reaction is:  $\text{NH}_3(\text{g}) + \text{HNO}_3(\text{g}) \rightleftharpoons \text{NH}_4\text{NO}_3(\text{s})$  for which we can write the extent of reaction as  $x = \nu_{\text{NH}_3} = \nu_{\text{HNO}_3} = \nu_{\text{NH}_4\text{NO}_3}$ .

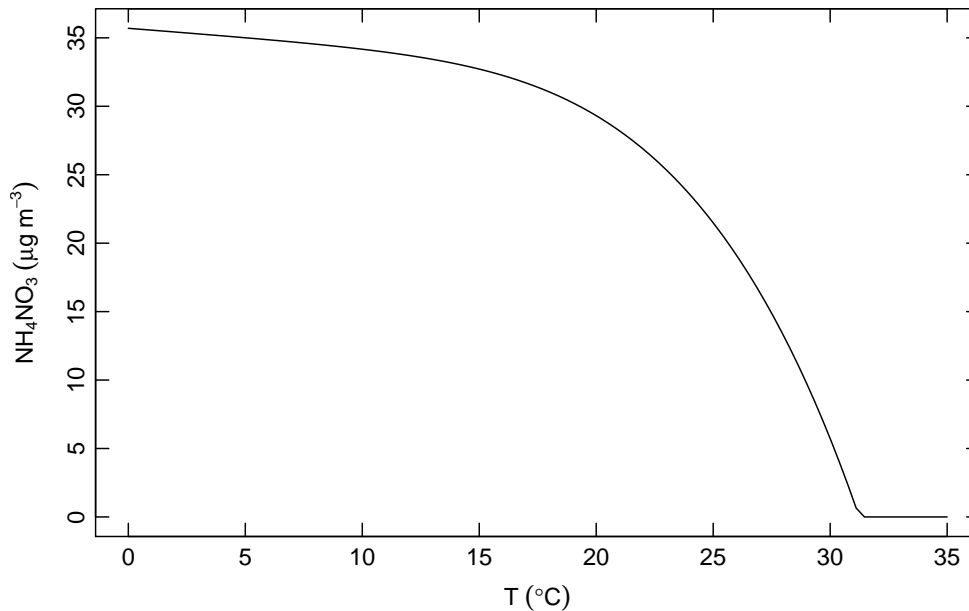
$\xi_{\text{NH}_3} \xi_{\text{HNO}_3}$  in excess of  $K_p$  will form  $\text{NH}_4\text{NO}_3(\text{s})$ . At equilibrium, the gas-phase concentration will be:

$$K_p = (\xi_{\text{NH}_3} - x)(\xi_{\text{HNO}_3} - x) \quad (1)$$

$x$  is the moles of  $\text{NH}_4\text{NO}_3(\text{s})$ , which can then be converted to units of aerosol mass concentration.

Check against temperature-dependent DRH (derived from Clausius-Clapeyron equation) to see if you should be using  $K_p$  for solid particles or aqueous particles. For solid particles,  $K_p = 10^{18} K_{\text{AN}(\text{s})}$ ; the equilibrium constant  $K_{\text{AN}(\text{s})}$  can be obtained from standard chemical potentials calculated at each temperature (use thermodynamic constants from table provided in lecture). For aqueous particles, use the figure provided in lecture to obtain the dissociation constant.

a)  $30\% \text{ RH} < \text{DRH} \rightarrow$  particles are solid. Obtain  $K_p$  for solid particles and solve eq. 1.

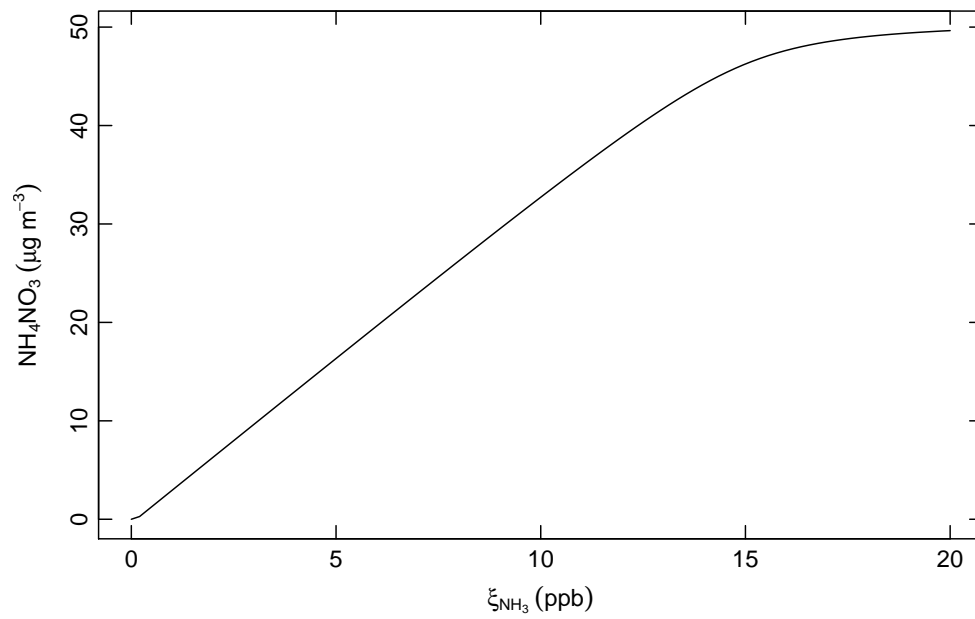


b)  $\text{RH} > \text{DRH} \rightarrow$  particles are aqueous. Read off  $K_p$  graphically (slide 49) for  $Y = 1$  (no sulfate in the system) and solve eq. 1.

- $\text{RH} = 70\%$ ,  $\text{NH}_4\text{NO}_3 \approx 21 \mu\text{g m}^{-3}$

- $RH = 85\%$ ,  $NH_4NO_3 \approx 26 \mu g m^{-3}$

c) Particles are solid again, so same as (a).



d) Many solutions can satisfy this condition.

e) The formation of aerosol ammonium nitrate is favored by low temperatures, high RH, and high total nitric acid and ammonia concentrations.