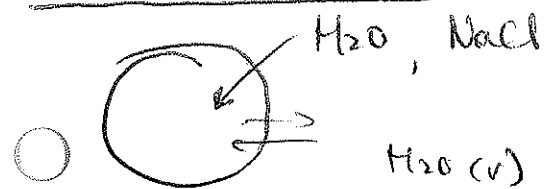


Another example:



What is the water content of a NaCl particle in equilibrium with water vapor of a given partial pressure (relative humidity, RH)?

Some assumptions / clarifications

RH > deliquescence RH. Express content as the mol fraction of water in the aerosol. Assume that the water condensing on particles is negligible compared to the total water vapor around. Also, assume ideal solution.

At equilibrium:

$$\mu_{H_2O(g)} = \mu_{H_2O(e)}$$

but:  $\mu_{H_2O(g)} = \mu_{H_2O(g)}^* + RT \ln y_{H_2O} P$

$$\mu_{H_2O(e)} = \mu_{H_2O(e)}^* + RT \ln X_{H_2O}$$

$y, x$  vary independently  
 that means they are uncoupled, i.e., mass conservation doesn't have to be used!

So:  $\mu_{H_2O(g)}^* + RT \ln y_{H_2O} P = \mu_{H_2O(e)}^* + RT \ln X_{H_2O}$

If we could only get "rid" of the reference potentials!

well... if the aerosol were pure water,

you would have:

$$\begin{aligned} \mu_{H_2O(g)} &= \mu_{H_2O(g)}^* + RT \ln(y_{H_2O} P)^{\text{saturation}} \\ \mu_{H_2O(l)} &= \mu_{H_2O(l)}^* + RT \ln X_{H_2O} \quad \leftarrow \ln 1 = 0 \right. \\ &= \mu_{H_2O(l)}^* \end{aligned} \quad \left. \vphantom{\mu_{H_2O(l)}} \right\} \Rightarrow$$

$$\mu_{H_2O(g)}^* - \mu_{H_2O(l)}^* = -RT \ln P_{H_2O}^{\text{sat}} \quad (2)$$

from (1):

$$\mu_{H_2O(g)}^* - \mu_{H_2O(l)}^* = RT \ln X_{H_2O} - RT \ln(y_{H_2O} P)$$

They are the same

$$\text{So: } -RT \ln P_{H_2O}^{\text{sat}} = RT \ln X_{H_2O} - RT \ln(y_{H_2O} P)$$

$$\ln \left( \frac{y_{H_2O} P}{P_{H_2O}^{\text{sat}}} \right) = \ln X_{H_2O}$$

$\leftarrow P_{H_2O}$

$$\text{So } \frac{P_{H_2O}}{P_{H_2O}^{\text{sat}}} = X_{H_2O} \Rightarrow \boxed{RH = X_{H_2O}}$$

relative humidity

The higher the RH, the more water in the particle!

### Implications

So, if you start off with a particle of dry diameter  $d_p$ . # of moles of NaCl in it are:

$$n_s = \frac{\pi}{6} d_p^3 \rho_s \frac{1}{M_s} ; m_s = \frac{\pi}{6} d_p^3 \rho_s$$

$\uparrow$  salt  $\uparrow$  mass of salt in dry particle.

Once water starts condensing, The particle begins to grow (b/c NaCl remains in particle and  $H_2O$  is added on it).

Assume a wet diameter of  $D_p$ , and The particle density is  $\rho$ .

Given that  $x_w = \frac{n_w}{n_w + n_s} = RH \Rightarrow$

$$\Rightarrow n_w = n_w(RH) + n_s(RH) \Rightarrow n_w = n_s \left( \frac{RH}{1 - RH} \right)$$

and The mass of water;  $m_w$

$$m_w = n_s \left( \frac{RH}{1 - RH} \right) \frac{1}{M_w} = m_s \left( \frac{RH}{1 - RH} \right) \left( \frac{M_s}{M_w} \right)$$

So the total amount of mass in particle is:

$$m_w + m_s = m_s \left[ 1 + \left( \frac{RH}{1 - RH} \right) \left( \frac{M_s}{M_w} \right) \right]$$

and The wet diameter of The particle is determined as

$$m_w + m_s = \frac{\pi}{6} D_p^3 \rho = m_s \left[ 1 + \left( \frac{RH}{1-RH} \right) \left( \frac{M_s}{M_w} \right) \right]$$

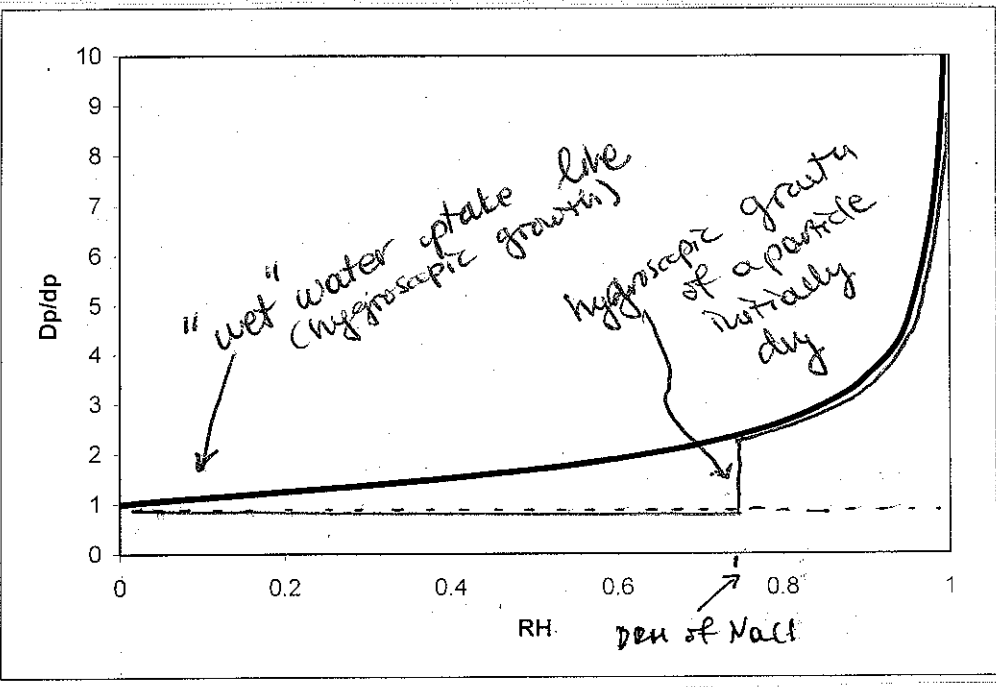
$$m_s = \frac{\pi}{6} d_p^3 \rho_s$$

$$\Rightarrow \cancel{\frac{\pi}{6}} D_p^3 \rho = \cancel{\frac{\pi}{6}} d_p^3 \rho_s \left[ 1 + \left( \frac{RH}{1-RH} \right) \left( \frac{M_s}{M_w} \right) \right] \Rightarrow$$

$$\Rightarrow D_p = d_p \left\{ \left( \frac{\rho_s}{\rho} \right) \left[ 1 + \left( \frac{RH}{1-RH} \right) \left( \frac{M_s}{M_w} \right) \right] \right\}^{1/3}$$

$\rho_s \sim 2150 \text{ kg m}^{-3}$  ;  $\rho \sim 1200 \text{ kg m}^{-3}$   
 $M_s = 58.5 \times 10^{-3} \text{ kg mol}^{-1}$  ;  $M_w = 18 \times 10^{-3} \text{ kg mol}^{-1}$

RH	Dp/dp
0	1
0.05	1.06928091
0.1	1.13031367
0.15	1.19035394
0.2	1.25124561
0.25	1.31403842
0.3	1.37962988
0.35	1.44895707
0.4	1.52310481
0.45	1.60340979
0.5	1.69159603
0.55	1.789978
0.6	1.90178995
0.65	2.03175629
0.7	2.18715021
0.75	2.37993164
0.8	2.63156861
0.85	2.98572742
0.9	3.55070327
0.95	4.72202889
0.99	8.65455657
0.999	19.064446



That is why sky is much "hazier" when its humid => particles swell alot and scatter light considerably!

So, knowledge of the amount of material, PM and gas-phase species (and  $T$ !) is important for predicting atmospheric PM and their impact on climate.

We need to solve all relevant thermodynamic reaction equations, coupled with conservation of mass, charge and knowing if water is present.  
 → Aerosol thermodynamic models do this!

TABLE 9.6 CHEMICAL REACTIONS OCCURRING IN ATMOSPHERIC AEROSOLS

Reaction	Equilibrium Constant Value		
	$K(298)$	$a$	$b$
$\text{NaCl(s)} + \text{HNO}_3(\text{g}) \rightleftharpoons \text{NaNO}_3(\text{s}) + \text{HCl(g)}$	3.96	5.50	-2.18
$\text{HSO}_4^- \rightleftharpoons \text{H}^+ + \text{SO}_4^{2-}$	$1.01 \times 10^{-2}$ ( $\text{mol kg}^{-1}$ )	8.85	25.14
$\text{NH}_3(\text{g}) + \text{HNO}_3(\text{g}) \rightleftharpoons \text{NH}_4^+ + \text{NO}_3^-$	$4.0 \times 10^{17}$ ( $\text{mol}^2 \text{kg}^{-2} \text{atm}^{-2}$ )	64.7	11.51
$\text{HCl(g)} \rightleftharpoons \text{H}^+ + \text{Cl}^-$	$2.03 \times 10^6$ ( $\text{mol}^2 \text{kg}^{-2} \text{atm}^{-1}$ )	30.21	19.91
$\text{NH}_3(\text{g}) + \text{HCl(g)} \rightleftharpoons \text{NH}_4^+ + \text{Cl}^-$	$2.12 \times 10^{17}$ ( $\text{mol}^2 \text{kg}^{-2} \text{atm}^{-2}$ )	65.08	14.51
$\text{Na}_2\text{SO}_4(\text{s}) \rightleftharpoons 2 \text{Na}^+ + \text{SO}_4^{2-}$	0.48 ( $\text{mol}^3 \text{kg}^{-3}$ )	0.98	39.57
$(\text{NH}_4)_2\text{SO}_4(\text{s}) \rightleftharpoons 2 \text{NH}_4^+ + \text{SO}_4^{2-}$	1.425 ( $\text{mol}^3 \text{kg}^{-3}$ )	-2.65	38.55
$\text{HNO}_3(\text{g}) \rightleftharpoons \text{H}^+ + \text{NO}_3^-$	$3.638 \times 10^6$ ( $\text{mol}^2 \text{kg}^{-2} \text{atm}^{-1}$ )	29.47	16.84
$\text{NH}_4\text{Cl(s)} \rightleftharpoons \text{NH}_3(\text{g}) + \text{HCl(g)}$	$1.039 \times 10^{-16}$ ( $\text{atm}^2$ )	-71.04	2.40
$\text{NH}_3(\text{g}) + \text{HNO}_3(\text{g}) \rightleftharpoons \text{NH}_4\text{NO}_3(\text{s})$	$3.35 \times 10^{19}$ ( $\text{atm}^{-2}$ )	75.11	-13.5
$\text{NaCl(s)} \rightleftharpoons \text{Na}^+ + \text{Cl}^-$	37.74 ( $\text{mol}^2 \text{kg}^{-2}$ )	-1.57	16.89
$\text{NaHSO}_4(\text{s}) \rightleftharpoons \text{Na}^+ + \text{HSO}_4^-$	$2.44 \times 10^4$ ( $\text{mol}^2 \text{kg}^{-2}$ )	0.79	4.53
$\text{NaNO}_3(\text{s}) \rightleftharpoons \text{Na}^+ + \text{NO}_3^-$	11.97 ( $\text{mol}^2 \text{kg}^{-2}$ )	-8.22	16.0

Where

$$K(T) = K(298) \exp \left\{ a \left( \frac{298}{T} - 1 \right) + b \left[ 1 + \ln \left( \frac{298}{T} \right) - \frac{298}{T} \right] \right\}$$