YOUR NAME: SOLUTIONS

AT 621
Atmospheric Chemistry

EXAM STATISTICS

Exam 2

AVERAGE 72.9

MEDIAN 72

STD. DEV. 19

Thursday,

November 20, 1997

Exam is 1 hour

THREE PROBLEMS

** Note point weighting assigned to each problem **

CLOSED BOOK

CLOSED NOTES

1. *[40 points]*

Assume that, at a particular sampling location, the atmospheric aerosol consists only of ammonium sulfate particles. Further, the size distribution is monodisperse (all particles have the same diameter).

The measurement indicates that there are 1000 particles cm^{-3} air.

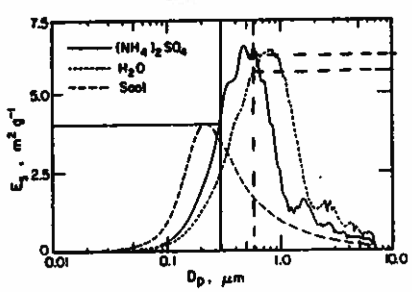
The size of the DRY particles (measured at very low relative humidity, *RH*) is 0.3 μm.

The density of dry ammonium sulfate is 1.76 g cm^{-3}.

The extinction coefficient, b_{ext}, is given by

$$b_{ext} = \int_0^\infty [E_a(m, Dp, \lambda) + E_s(m, Dp, \lambda)] f(Dp) dDp$$

The following figure may be used:



refractive index of $(NH_4)_2SO_4$ $= 1.53 + 0i$

water $= 1.33 + 0i$

$(\lambda \sim 0.53\ \mu m)$

20 (a) Calculate the value of the extinction coefficient for the DRY aerosol.

- For ammonium sulfate, there is only a real part of the refractive index, so $b_{ext} = b_{sp}$.
- Since all particles are the same size,

$$b_{sp} = E_s(D_p)\, M\, 10^6$$

where M = mass of particulate matter in $\frac{g}{cm^3\, air}$

and $10^6 \frac{cm^3}{m^3}$ makes $b_{sp}\ [=]\ m^{-1}$

(Problem 1a)

From the figure, $E_s(D_p = 0.3\ \mu m) = 4.0\ \frac{m^2}{g}$

Thus

$$b_{sp} = 4.0\ \frac{m^2}{g} \cdot M \cdot 10^6$$

to get M:

$$M = \frac{\pi}{6} \int_0^\infty \rho\, D_p^3\, n(D_p)\, dD_p$$

$$M = \frac{\pi}{6} \rho\, D_p^3\, N \quad \text{since monodisperse}$$

$$M = \frac{\pi}{6}\ 1.76\ \frac{g}{cm^3}\ (0.3 \times 10^{-4})^3\ cm^3\ \frac{1000}{cm^3\ air}$$

$$M = 2.5 \times 10^{-11}\ \frac{g}{cm^3\ air}$$

$V = 1.41 \times 10^{-14}\ \frac{cm^3}{particle}$

$$b_{sp} = 4.0\ \frac{m^2}{g} \times 2.5 \times 10^{-11}\ \frac{g}{cm^3\ air} \times 10^6\ \frac{cm^3}{m^3}$$

$$b_{sp} = 1.0 \times 10^{-4}\ m^{-1}$$

(Problem 1b)

20 (b) When the particles are exposed to a higher RH = 90%, water mass is added to the particles, in a ratio of 3 g water per g of ammonium sulfate. The optical properties of the solution are close to that of water.

Calculate the value of the extinction coefficient at RH = 90%.

The same formula applies, except M is increased and D_p is increased.

$$M(RH=90\%) = M_{dry} + M_{water} = M_{dry} + \frac{3\ \text{g water}}{\text{g dry}} \cdot M_{dry}$$

$$= 4 \cdot M_{dry}$$

$$= 1 \times 10^{-10} \frac{\text{g}}{\text{cm}^3\ \text{air}}$$

$$M = \frac{\pi}{6} \rho D_p^3 N$$

$$D_p^3 = \frac{6}{\pi} \frac{1}{\rho} \frac{M}{N}$$

(M ← new value; N ← still 1000 cm^{-3}; ρ ← should be adjusted)

OR

$$\frac{M(RH=90\%)}{M_{dry}} = \frac{\frac{\pi}{6}\ \rho_{90\%}\ N_{90\%}\ D_{p_{90\%}}^3}{\frac{\pi}{6}\ \rho_{dry}\ N_{dry}\ D_{p_{dry}}^3}$$

$$\frac{D_{p_{90\%}}^3}{D_{p_{dry}}^3} \approx \frac{4\ M_{dry}}{M_{dry}} \frac{\rho_{dry}}{\rho_{90\%}}$$

(ρ_{dry} → 1.76; $\rho_{90\%}$ → ≈ 1 approx. as water ρ)

(Problem 1b)

$$\frac{D_{p_{90\%}}}{D_{p_{dry}}} = (4 \times 1.76)^{1/3} = 1.916$$

$$D_{p_{90\%}} \simeq 0.57\ \mu m$$

$$E_s(D_p \approx 0.57\mu m) = 5.8 \frac{m^2}{g} \ *$$

(use water curve)

$$b_{sp} = 5.8 \frac{m^2}{g} \times 1 \times 10^{-10} \frac{g}{cm^3\ air} \times 10^6 \frac{cm^3}{m^3}$$

$$b_{sp} = 5.8 \times 10^{-4}\ m^{-1}$$

* If we used curve for $(NH_4)_2SO_4$, get $E_s \sim 6.3 \frac{m^2}{g}$ (still pretty close at this size)

b_{sp} has increased by a factor of ≈ 6 even though mass has only increased by factor of 4. This is because the particles were grown into a more efficient size range for scattering.

2. *[40 points]*
The reactions for formaldehyde dissolving in cloud water are as follows:

$HCHO(g) \rightleftarrows HCHO(aq)$ $\quad H_f$

$HCHO(aq) \rightleftarrows H_2C(OH)_2(aq)$ $\quad K_1$

where H_f and K_1 are equilibrium constants.

30 (a) Derive the effective Henry's Law constant for formaldehyde.

H_{eff} is in the form

$$H_{eff} = f \cdot H_F \quad \text{where } f > 1$$

or $[HCHO]_{total}^{aq} = H_{eff}\, p_{HCHO}$

$$[HCHO(aq)]_{total} = [HCHO(aq)] + [H_2C(OH)_2(aq)]$$

$$H_F = \frac{[HCHO(aq)]}{p_{HCHO}}$$

$$K_1 = \frac{[H_2C(OH)_2(aq)]}{[HCHO(aq)]} = \frac{[H_2C(OH)_2(aq)]}{H_F\, p_{HCHO}}$$

$$[HCHO(aq)]_{total} = H_F\, p_{HCHO} + K_1 H_F\, p_{HCHO}$$

(Problem 2, continued)

$$[HCHO(aq)]_{total} = \underbrace{H_F(1 + K_1)}_{H_{eff}}\, p_{HCHO}$$

$f = 1 + K_1 > 1$ always

10 (b) How does the dissolution of formaldehyde depend upon pH?

from above, $f = 1 + K_1 \neq f(pH)$

So <u>The dissolution is independent of pH</u>

This is reasonable since formaldehyde does not release an H^+ or OH^- upon dissolution. It is neither an acid nor base.

3. *[20 points]*
Short answers:

4 (a) If two clouds have the same chemical conditions, but one has a much larger liquid water content, how do you expect this to alter the amount of S(IV) to S(VI) conversion that takes place in a m³ of air?

More conversion will take place in the cloud with higher LWC. This is because aqueous concentrations $\left(\frac{\text{moles S(IV)}}{\text{l water}}\right)$ will be similar but the higher LWC cloud has more $\frac{\text{l water}}{\text{l air}}$ ⇒ more reactor volume.

4 (b) For the following reactions:

$$BrO + ClO \rightarrow Br + Cl + O_2$$
$$Br + O_3 \rightarrow BrO + O_2$$
$$Cl + O_3 \rightarrow ClO + O_2$$

What is the significance of these reactions? Do they enhance or slow down ozone destruction?

These show a coupling between Br + Cl cycles. They enhance O_3 destruction because the BrO and ClO can react with each other to produce Br, Cl to attack O_3 directly, rather than destroying odd oxygen by BrO + O and ClO + O reactions.

4 (c) What is the significance of the following reactions:

$$NO_2 + O_3 \rightarrow NO_3 + O_2$$
$$NO_3 + NO_2 + M \rightarrow N_2O_5 + M$$

They form reservoir species NO_3 + N_2O_5. This limits O_3 destruction because NO, NO_2 is tied up and not available to participate in catalytic cycles.

(Problem 3, continued)

4 (d) The following sequence is a "null cycle" for ozone:

$$NO + O_3 \rightarrow NO_2 + O_2$$
$$NO_2 + h\nu \rightarrow NO + O$$

What alternative reactions might occur (i.e., which of these has a competing reaction) that would change this to an ozone loss pathway?

The first reaction destroys O_3. It can be followed by $NO_2 + O \rightarrow NO + O_2$ which destroys odd oxygen and regenerates NO. $NO_2 + h\nu \rightarrow NO + O$ actually regenerates both NO and odd oxygen.

4 (e) Explain the difference(s) between Type I and Type II PSCs.

Type I: generally smaller in size ($D_p \lesssim 1\ \mu m$)
form at warmer T's
composed of nitric acid + water

Type II: larger crystals (10 - 100 μm)
form only at colder T's (<195 K)
composed largely of water (ice)