

ASL735 (Atmospheric Chemistry and Air Pollution)  
Semester-I AY 2017-18  
Major Exam (Nov 19, 2017)  
Time 2 hours

Total Marks = 30

Answer either Q1 or (Q2 + Q3). If you have missed minor-1 or minor-2, answer Q1, Q2, and Q3.

**Q1.** The 1987 Montreal protocol was the first international agreement to control emissions of chlorofluorocarbons (CFCs) harmful to the ozone layer. It was subsequently amended (London 1990, Copenhagen 1992) to respond to the increased urgency created by the discovery of the Antarctic ozone hole. In this problem we compare the effectiveness of the original and amended protocols. We focus on CFC-12, which has an atmospheric lifetime of 100 years against loss by photolysis in the stratosphere. We start our analysis in 1989 when the Montreal protocol entered into force. In 1989 the mass of CFC-12 in the atmosphere was  $m = 1.0 \times 10^{10}$  kg and the emission rate was  $E = 4 \times 10^8$  kg/yr.

- The initial Montreal protocol called for a 50% reduction of CFC emissions by 1999 and a stabilization of emissions henceforth. Consider a future scenario where CFC-12 emissions are held constant at 50% of the 1989 values. Show that the mass of CFC-12 in the atmosphere would eventually approach a steady state value  $m = 2 \times 10^{10}$  kg, higher than the 1989 value. Explain briefly why the CFC-12 abundance would increase even though its emission decreases.
- The subsequent amendments to the Montreal protocol banned CFC production completely as of 1996. Consider a scenario where CFC-12 emissions are held constant from 1989 to 1996 and then drop to zero as of 1996. Calculate the masses of CFC-12 in the atmosphere in years 2050 and 2100. Compare with the 1989 value.

(Marks = 4 + 4 = 8)

**Q2.** Considering that the hydroxyl radical OH is absolutely essential for the ability of the troposphere to cleanse itself from harmful trace gases (such as for instance  $\text{SO}_2$ ,  $\text{NO}_x$  and CO) it is of great interest to examine to what extent human activities have affected the global OH concentrations. If, at the same time as we emit huge quantities of air pollutants, we also cause [OH] to decrease, then we are in real trouble. Ice cores drilled in the ice sheets of Greenland and Antarctica have shown to be useful for constraining historic [OH]. Scientists are able to measure the concentration of certain stable gases such as methane  $\text{CH}_4$  and formaldehyde HCHO in bubbles of gas captured in the ice as it formed. The ratios between various hydrogen and oxygen isotopes reveal even the temperature of the snow that once fell. Dating can be made using different methods, including  $^{14}\text{C}$ .

The main sink for formaldehyde HCHO in the Arctic is photolysis, with an average reaction rate constant  $k_1 = 1.0 \times 10^{-5} \text{ s}^{-1}$ . Oxidation of methane  $\text{CH}_4$  via OH is the only HCHO source of importance in the Arctic. The temperature dependent rate constant for this reaction is  $k_2 = 2.0 \times 10^{12} \exp(-1700/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , where T is the temperature in K.

- (i) Derive an expression for finding out the concentration of [HCHO] as a function of [CH<sub>4</sub>] and [OH].
- (ii) The table below shows the results of measurements made on Greenland ice cores that are representative of various time periods: present, pre-industrial (year 1800)

	[CH <sub>4</sub> ] ppbv	[HCHO] ppbv	T (K)
Present	1700	0.10	260
Pre-industrial	740	0.05	260

Calculate [OH] (molecules/cm<sup>3</sup>) over Greenland during each time period. How do you interpret the difference in [OH] between pre-industrial time and present?

(Marks = 2 + 1 + 1 = 4)

**Q3.** The radioactive isotope <sup>210</sup>Pb is formed from decay of <sup>222</sup>Rn, and condenses immediately on existing aerosol particles. <sup>222</sup>Rn is emitted from the ground in land areas with the flux (e) of 1.0 atoms/cm<sup>2</sup>/s, whereas the emissions from the sea are zero. Land covers 30% (f<sub>A</sub>) of the earth's surface. The radioactive decay forming <sup>210</sup>Pb is the only sink of <sup>222</sup>Rn. (half-life 3.8 days). <sup>210</sup>Pb is removed from the atmosphere by radioactive decay (half-life 23 years) and aerosol deposition. The total mass of <sup>210</sup>Pb in the troposphere is 380 g.

Calculate the residence time with respect to deposition of <sup>210</sup>Pb-containing aerosol particles in the troposphere. Assume steady state. [Hint: For a first order reaction, t<sub>1/2</sub> = 0.693 / k]

(Marks = 4)

Answer any two of the next three questions (Q4 to Q6). If you have missed minor-1 or minor-2, answer Q4, Q5 and Q6.

**Q4.** Explain in a few sentences whether you agree or disagree with each statement below. Support your position with equations or calculations when appropriate.

- Dust single scattering albedo decreases with higher amount of hematite content.
- For spherical particles, the Mie theory can be used for any aerosol size and at any wavelength of the solar spectrum.
- The sky appears as grey in polluted environment due to Mie scattering.
- Single scattering albedo of internally mixed BC and sulfate is higher than externally mixed BC and sulfate.

(Marks = 4)

**Q5.** Aerosol optical depth values for two different cities (located far from any sea or continental boundary) with similar population, anthropogenic activities are as follows

Wavelength (μm)	0.38	0.44	0.5	0.68	0.87	1.02
City-1	0.53	0.49	0.44	0.3	0.25	0.20
City-2	0.51	0.49	0.47	0.4	0.35	0.33

Chemical analysis of aerosols collected from both these cities are found to consist of varying amounts of Sulfate, Black Carbon (BC), Organic Carbon (OC), Dust, and Sea-Salt.

Microphysical properties of these aerosol species in their dry state is as follows

Table 1. Microphysical Properties of Aerosol Components in Dry State<sup>a</sup>

Component	$\sigma$ ( $\mu\text{m}$ )	$r_{\text{modeN}}$ ( $\mu\text{m}$ )	$r_{\text{modeV}}$ ( $\mu\text{m}$ )	$\rho$ ( $\text{g}/\text{cm}^3$ )
Sulfate (SI1)	2.0	0.05	0.17	1.77
Black carbon (BC)	1.8	0.04	0.095	1.0
Organic carbon (OC)	1.49	0.085	0.126	1.8
Small dust (Ds1)	2.0	0.38	1.26	2.5
Large dust (Ds2)	1.6	2.6	4.517	2.6
Sea salt accumulation (SS1)	1.59	0.13	0.22	2.16
Sea salt coarse (SS2)	2.0	0.74	2.46	2.16

<sup>a</sup>Here the size parameters  $\sigma$  (width of the distribution),  $r_{\text{modeN}}$  (mode radius for number size distribution) and  $r_{\text{modeV}}$  (mode radius for volume size distribution) correspond to lognormal size distribution of aerosols and  $\rho$  is the mass density of aerosol particles

Which of the two cities has higher sulfate/dust ratio. Justify your answer.

(Marks = 1 + 3 = 4)

**Q6.** An aerosol sampler is designed in such a way that it captures only those aerosols with aerodynamic diameter smaller than  $2.5 \mu\text{m}$ . If all the particles captured by the sampler are spherical with a density of  $2.6 \text{ g}/\text{cm}^3$  and aerodynamic diameter  $2.5 \mu\text{m}$ , what is the geometric diameter of these particles?

[Hint: Settling velocity of particles is given by

$$v_r = \frac{D_p^2 \rho_p g C_r}{18\mu}$$

where  $D_p$  is the diameter and  $\rho_p$  is the density of the particle,  $\mu$  = dynamic viscosity of air ( $1.983 \times 10^{-5} \text{ N s}/\text{m}^2$ ). Assume the slip correction factor to be unity for  $D_p \sim 2.5 \mu\text{m}$ .

(Marks = 4)

**Answer any two of the next four questions (Q7 to Q10). If you have missed minor-1 or minor-2, answer any three of the next four questions (Q7 to Q10).**

**Q7.** If  $Q_{\text{ext}}(m, x)$  is the extinction efficiency of aerosol with refractive index  $m$  ( $n + ik$ ) and size parameter  $x$ , write down expressions for calculating the extinction coefficient and aerosol optical depth of a poly-disperse aerosol distribution at wavelength  $\lambda$ .

(Marks = 2)

**Q8.** Explain in a few sentences whether you agree or disagree with each statement below. Support your position with equations or calculations when appropriate.

- a) Single scattering albedo of aerosols decrease with increasing absorption.

b) The sky appears as grey in polluted environment due to Mie scattering.

(Marks = 2)

**Q9.** Answer the following questions in a few sentences. Support your answer with equations, calculations or proper explanations when appropriate.

- a) Which aerosol will have higher scattering phase function between Sulfate and dust?  
 b) Why do clouds appear white and sky appears blue over pristine locations?

(Marks = 2)

**Q10.** If the aerosol optical depths and single scattering albedos of BC (black carbon), OC (organic carbon), sulfate, dust, and sea-salt aerosols at 0.5  $\mu\text{m}$  and RH 50% over some location on some day are as follows

	BC	OC	Sulfate	Dust	Sea-salt
Single scattering albedo	0.4	0.91	0.99	0.85	0.98
Aerosol optical depth	0.05	0.15	0.2	0.15	0.05

Compute the aerosol optical depth and single scattering albedo of all the aerosols together assuming them to be externally mixed.

(Marks = 2)

**Answer any three of the next six questions (Q11 to Q16). If you have missed minor-1 or minor-2, answer any five of the next six questions (Q11 to Q16).**

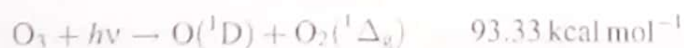
**Q11.** What are typical lifetimes for nucleation, accumulation mode, and coarse aerosols? What are the dominant physical processes control the lifetimes of nucleation, accumulation mode, and coarse aerosols in the lower troposphere?

(Marks = 3)

**Q12.** What is ozone hole and explain its formation mechanism?

(Marks = 3)

**Q13.** The enthalpy changes for the following photodissociation reactions are



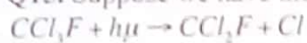
Estimate the maximum wavelengths at which these reactions can occur.

(Marks = 3)

**Q14.** What is the source of singlet excited state oxygen atom involved in the catalytic destruction of ozone in the stratosphere? Would you expect  $[O]$  and  $[O_3]$  concentrations in the stratosphere to vary with time of day, and if so how?

(Marks = 1+2=3)

**Q15.** Suppose we have the following sequence of reactions:



These two reactions dictate the stratospheric production and loss of chlorine atoms.

- Write down the rate equation for Cl.
- Find the mathematical expression for the steady-state concentration of Cl.
- What are the major sources of methane emission in the troposphere?

(Marks = 1+1+1=3)

**Q16.** For the simple decomposition reaction



the rate law is  $\text{rate} = k[AB]^2$ , and  $k=0.2 \text{ L/mol}\cdot\text{s}$ . How long will it take for  $[AB]$  to reach  $1/3$  of its initial concentration of  $1.50\text{M}$ ?

(Marks =1+2= 3)