

ENV-320 Exam
Atmospheric Chemistry and Physics
Spring 2014

Problems 1 to 3 are related to atmospheric physics (50 points) and problems 4 to 8 are related to atmospheric chemistry (50 points) for a total of 100 points.

Atmospheric physics

Problem 1: Fair weather idealized ABL

In atmospheric chemistry (see below), certain parts of the atmosphere are often regarded as a well-mixed and closed box. The daytime atmospheric boundary layer (ABL) in fair weather conditions can be seen as such a well-mixed box, in which a lot of the photochemical smog (ozone) production happens. In the following, we will look at some characteristics of the daytime fair-weather ABL.

Problem 1a: (5pts) Which energy fluxes drive the growth of the ABL against a slightly stable background (free troposphere) stratification? Qualitatively describe, how a convective ABL develops in these conditions.

Problem 1b: (7pts) Assume you have a sonic anemometer which measures at high frequency (20 Hz) temperature and three-dimensional wind speed. Assume you measure these (hypothetical) temperatures and vertical wind speeds:

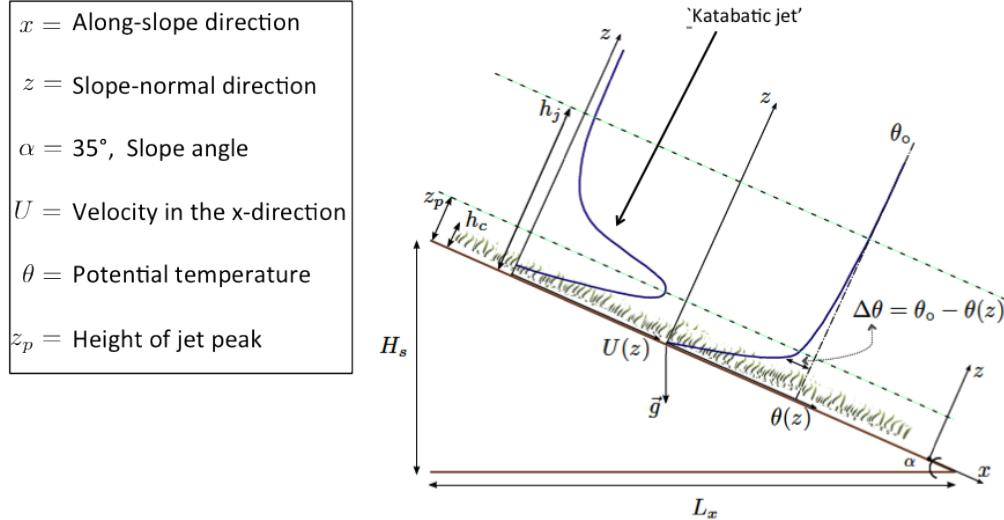
T ($^{\circ}\text{C}$): 20, 25, 28, 25, 23, 18, 17, 17, 13, 14.....
w (m s^{-1}): 0.05, 0.1, 0.1, 0.05, 0.05, -0.05, -0.1, -0.1, -0.05, -0.05.....

Assume that under stationary conditions, the values given above repeat itself indefinitely and calculate the surface sensible heat flux $q_s = \rho c_p \overline{w' T'}$ with a suitable assumption for the density of air (1 kg m^{-3}) and the heat capacity ($1000 \text{ J kg}^{-1} \text{ K}^{-1}$).

Problem 1c: (6pts) Estimate the growth rate (velocity) of a convective ABL given the heat flux just calculated and assuming a ball parameter of 0.2 and a strength of the capping inversion of $3 \text{ }^{\circ}\text{C}$. If you could not solve 1c, just assume a reasonable sensible heat flux value.

Problem 2: Nighttime katabatic slope flow

Now we leave flat terrain and look at the situation over slopes, in particular at nighttime. In class we have talked about katabatic and anabatic winds. Consider a beautiful, clear, summer night in the Alps when synoptic forcing (large-scale weather patterns) is weak. Under these conditions katabatic flows are likely to form over the slopes as shown in the schematic.



Problem 2a: (3 pts) Why are clear skies (no clouds) and weak synoptic forcing important to the formation of these flows?

Problem 2b: (3 pts) Why does the air flow *down* the slope and why is there a peak in downslope velocity?

Problem 2c: (3 pts) Is the atmospheric boundary layer unstable, stable or neutral and what is a reasonable lapse rate for potential temperature for this situation? (choose one: 6.4 °C/km, 10 °C/km, -5 °C/km)

Problem 2d: (3 pts) Where are the maximum and the minimum *magnitudes* of the wind shear along the z direction?

Problem 2e: (3 pts) Identify regions in the katabatic jet layer where the momentum fluxes are positive and negative (if such a region exists).

Problem 2f: (3 pts) Identify regions in the katabatic jet layer where the heat fluxes are positive and negative (if such a region exists).

Problem 2g: (7 pts) Using the simplified equation for streamwise momentum

$$\frac{\partial \overline{u'w'}}{\partial z} = g \frac{\Delta\theta}{\theta_o} \sin(\alpha)$$

and assuming a linear potential temperature profile (given below) and that the momentum flux at the surface is known constant, derive an equation that could be used to estimate the location (height) of the jet $\Delta\theta(z) = \theta_o(1 - z/h_J)$ peak, z_p . Hint: use the friction velocity to estimate the turbulent momentum flux near the wall.

Problem 3: Large scale energy transport (7 pts)

Describe the main S-N and W-E energy redistribution mechanisms that act on the Northern Hemisphere (do not consider changes in the ITCZ position)

Atmospheric chemistry

Recall mass balance for species X in the (well-mixed) box:

$$\frac{dm}{dt} = F_{\text{in}} - F_{\text{out}} + E + P - L - D$$

where m is the concentration of X , F_{in} and F_{out} are transport rates into and out of the control volume; E , P , L , D are rates of emission, production, loss, and deposition. The lifetime τ of X with respect to various sinks are defined as

$$\begin{aligned}\tau_{\text{out}} &= \frac{m}{F_{\text{out}}} && \text{(export)} \\ \tau_c &= \frac{m}{L} && \text{(chemical loss)} \\ \tau_d &= \frac{m}{D} && \text{(deposition)}\end{aligned}$$

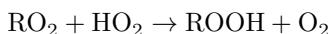
Hint: this conservation equation can be formulated such that m is in mass, molar, or molecular concentrations.

Problem 4: Tropospheric ozone chemistry

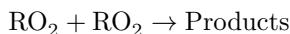
Recall the role of VOCs in ozone chemistry, which occurs alongside the chemistry involving CO. R represents a hydrocarbon fragment; the parent hydrocarbon is RH. Peroxy radicals RO_2 can oxidize NO to form NO_2 .



RO_2 can be removed by reaction with HO_2



or the self-reaction



Problem 4a: (5 pts) Write an argument in favor of this statement: “The relative magnitude of the $\text{RO}_2 + \text{NO}$ reaction compared to the $\text{RO}_2 + \text{HO}_2$ or $\text{RO}_2 + \text{RO}_2$ reactions is a critical factor in ozone formation in the troposphere.”

Problem 4b: (quantitative 5 pts) Let us use C_2H_5 for R in this example (parent hydrocarbon of this fragment is ethane, C_2H_6). Relative magnitudes of the reaction of $\text{C}_2\text{H}_5\text{O}_2$ with NO, HO_2 , $\text{C}_2\text{H}_5\text{O}_2$ under polluted concentrations are given by their respective lifetimes under peak concentrations at 298 K:

Reaction	Mechanism	τ_c (seconds)	Peak concentration
1	$\text{C}_2\text{H}_5\text{O}_2 + \text{NO}$	0.2	20 ppb of NO
2	$\text{C}_2\text{H}_5\text{O}_2 + \text{HO}_2$	1.3×10^2	40 ppt of HO_2
3	$\text{C}_2\text{H}_5\text{O}_2 + \text{C}_2\text{H}_5\text{O}_2$	1.6×10^4	40 ppt $\text{C}_2\text{H}_5\text{O}_2$

Recall that loss for a second order reaction between X and Y is written as

$$L = k_c[X][Y]$$

where k_c is a reaction rate constant and $[.]$ denotes molecular concentrations. What are the respective rate constants (in units of $\text{cm}^3 \text{molec}^{-1} \text{s}^{-1}$) for reactions 1–3?

Problem 4c: (5 pts) The rate constant for the $\text{NO} + \text{HO}_2$ reaction is $8.1 \times 10^{-12} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ at 298 K. Recall that VOCs comprise a large number of compounds, of which C_2H_6 is only example. What can you say about role of VOCs relative to HO_2 in tropospheric ozone production?

Problem 4d: (5 pts) We used the following equation to calculate the ozone production efficiency (OPE) on the CO-NO_x-O₃ system:

$$OPE = \frac{P_{O_3}}{L_{NO_x}} = \frac{k_{HO_2+NO}[HO_2][NO]}{k_{OH+NO_2}[OH][NO_2]}$$

Can this same equation provide a meaningful estimate of OPE for the VOC-NO_x-O₃ system? Justify your answer.

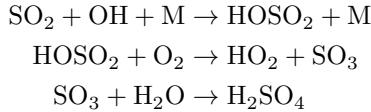
Problem 5: Sulfate aerosol chemistry and physics

Recall that the steady-state molar flow of substance *A* to a particle with radius R_p during condensation/evaporation is given by

$$J_A = 4\pi R_p D_A (c_{\infty,A} - c_{eq,A}) f(Kn, \alpha)$$

where D_A is the gas-phase diffusivity of *A*, $c_{\infty,A}$ and $c_{eq,A}$ are the ambient and equilibrium concentrations of *A*, and $f(Kn, \alpha)$ is a coefficient accounting for the Knudsen number Kn and mass accommodation coefficient α .

The daytime sulfuric acid production in the gas-phase by the following reactions:



Problem 5a: (quantitative 5pts) As an approximation, assume that you have 1000 cm⁻³ ammonium sulfate (NH₄)₂SO₄ particles that are 100 nm in spherical diameter. If chemical production and heterogeneous condensation are the two dominant mechanisms, what is the production rate (in molec cm⁻³ s⁻¹) of H₂SO₄ required to sustain a gas-phase concentration of 1 ppt of H₂SO₄? Assume the following constant values during this process:

$$\begin{aligned} D_{H_2SO_4} &= 0.1 \text{ cm}^2 \text{ s}^{-1} \\ f(Kn, \alpha) &\approx 0.4 \\ c_{eq,H_2SO_4} &\approx 0 \text{ molec cm}^{-3} \end{aligned}$$

Problem 5b: (5pts) What is another major mechanism for the formation of sulfate aerosols from SO₂?

Problem 5c: (5pts) If sulfate aerosols are injected into the stratosphere, how might this action affect the magnitude of a) radiative forcing, b) stratospheric ozone concentrations, and c) tropospheric ozone concentrations?

Problem 6: (5pts) Recall that the saturation ratio is defined by $S = e/e_s$, where e and e_s are the ambient and saturation vapor pressure of water, respectively. In what environments are supersaturated conditions ($S > 1$) be created?

Problem 7: (5pts) Name two mechanisms by which (a) liquid cloud droplets and (b) ice cloud particles grow and form precipitation.

Problem 8: (5pts) (a) How has reduction in CFC emissions due to the Montreal Protocol affected stratospheric ozone concentrations? (b) The Montreal Protocol was first enacted in 1987, so why has the response in expected changes to stratospheric ozone concentrations not been observed immediately?