Physics and Chemistry of the Atmosphere Exam
Spring 2017

This exam consists of 9 questions for a total of 60 points (30 physics / 30 chemistry). No internet access or communication with classmates during the exam is allowed.

PHYSICAL CONSTANTS:

- Specific heat at constant pressure, c_p : 1004 J $\mathrm{K}^{-1}\,\mathrm{kg}^{-1}$
- Gas Constant for 1 kg of dry air, R_D: 287.0 J $\mathrm{K}^{-1}\,\mathrm{kg}^{-1}$
- Stefan-Boltzmann constant, σ: 5.67 $\times 10^{-8}$ $\mathrm{W\,m^{-2}\,K^{-4}}$

USEFUL EQUATIONS AND SYMBOL DEFINITIONS:

$$m = N\rho_p \frac{4}{3}\pi R_p^3$$

$$\tau_s = \frac{1}{4\pi N R_p D_A\, f(Kn,\alpha)} = \frac{\rho_p R_p^2}{3D_A\, f(Kn,\alpha)\, m}$$

$$f(Kn,\alpha) = \frac{0.75\alpha(1+Kn)}{Kn^2 + Kn + 0.283Kn\alpha + 0.75\alpha}, \quad \text{where} \quad Kn = \frac{2\lambda}{D_p}$$

Symbol	Definition
m	mass concentration of aerosol population
τ_s	characteristic timescale for condensation/evaporation
N	number concentration of aerosol population
ρ_p	mass density of a particle
R_p	particle radius
D_p	particle diameter
λ	mean free path of gas molecule
α	mass accommodation coefficient
f	Fuchs-Sutugin correction factor
D_A	diffusion coefficient of gas molecule

QUESTION I

For meteorological forecasting it has been useful to take local measurements of pressure at the earth's surface. In a mountainous terrain such as Switzerland, elevation has the dominant influence on pressure. Therefore, in order to be able to compare pressure measurements at different locations, pressure is often "reduced" to sea level, i.e. it is calculated what would be the sea level pressure corresponding to the pressure measured at some elevation. This then facilitates the drawing of weather maps and to study the distribution of high and low pressure systems.

[7 points]. (A): In class and in the book, we often used the first law of thermodynamics in the form: $\mathrm{d}q = c_p \mathrm{d}T - (1/\rho)\,\mathrm{d}p$, where q is heat, T is temperature, ρ is density and p is the pressure of the system. Use the assumption of an adiabatic air parcel movement to derive a formula that relates pressures and temperatures at two levels, one being sea level and one being at elevation z. Consider air to behave as an ideal gas. *Hint: The same reasoning has been used for the definition of potential temperature.*

[7 points]. (B): Calculate the sea-level pressure for a location in Switzerland at an elevation of 1500 m, where you also measure a local air temperature of 10^{o} C. You can assume the atmosphere to be well-mixed with a dry adiabatic lapse rate of 0.0098 K/m.

*** SOLUTION ***

[7 points]. (A): Using the assumption of adiabatic air movement, $\mathrm{d}q = 0$. Thus, $c_p \mathrm{d}T = (1/\rho)\,\mathrm{d}p$. Using the ideal gas law, $p = \rho\, R_d\, T$, we get,

$$\left(\frac{c_p}{R_D}\right)\frac{\mathrm{d}T}{T} = \frac{\mathrm{d}p}{p}\,. \qquad (1)$$

Integrating the above equation between (p_0, T_0) and (p, T), we get the following expression for p_0.

$$p_0 = p\left(\frac{T}{T_0}\right)^{-\frac{c_p}{R_D}} \qquad (2)$$

[7 points]. (B): Using the dry adiabatic lapse rate which has been provided, for $T = 10^{o}C$, $T_0 = 24.7^{o}C$. The value of the physical constants c_p and R_D have been provided to the students in the question paper. Thus, for a value of $P = 850hPa$, P_0 **can be found using Equation 2 to give 1014.6453 hPa** .

QUESTION II

[5 points]. (A): Consider the situation in Figure 1. Parallel beam solar radiation is incident upon Earth. **Compute the temperature of Earth** such that it is in radiative equilibrium. Assume that Earth has an albedo value of 0.30. Incoming solar radiation flux $F_S = 1368\ \mathrm{Wm}^{-2}$. Emmisivity is equal to 1.

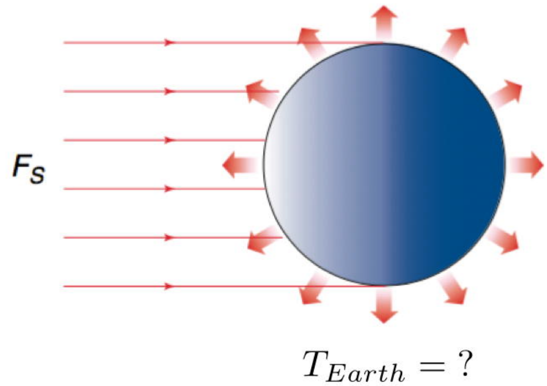

Figure 1: Solar radiation directly incident on Earth

[5 points]. (B): In Part (A), we considered an extremely simple system where Earth interacts directly with solar radiation. However, in reality, there is a layer of atmosphere between space and Earth's surface. Consider the situation shown in Figure 2. The gray band is a toy atmosphere we have now introduced. Thus, the atmosphere is a spherical shell enclosing earth. This atmosphere has the following properties :

- The atmosphere DOES NOT interact with shortwave radiation, i.e, for shortwave radiation, the atmosphere is completely transparent.
- The atmosphere acts as a perfect blackbody for longwave radiation
- The altitude and the depth of the atmosphere is NOT important.
- The atmosphere has the same surface area as Earth on both it's inner and outer surface.

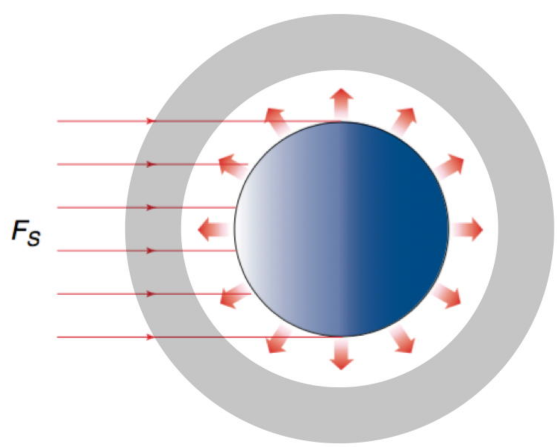

Figure 2: Earth-atmosphere system: Solar radiation passing through atmosphere and then interacting with Earth

Compute the temperature of Earth such that Earth as well as the atmosphere is in radiative equlibrium ?

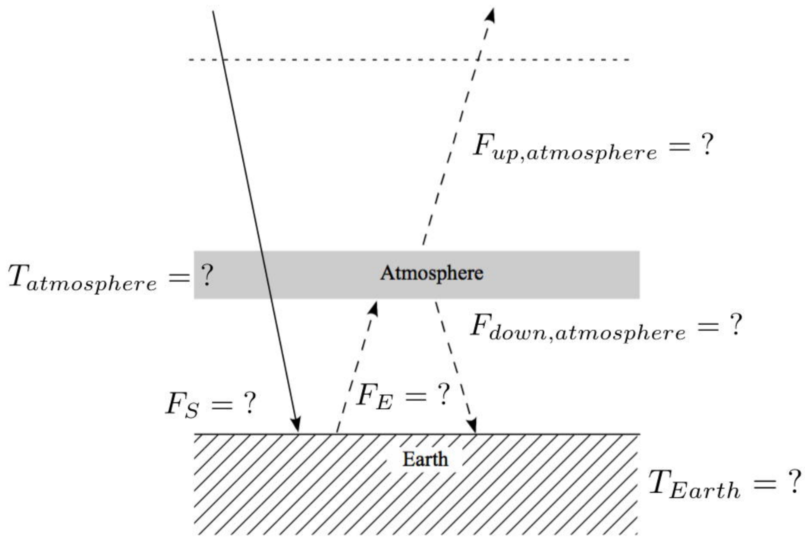

Figure 3: A zoomed view of the Earth-atmosphere system. Think about all the unknown quantities.

Continue using 0.30 as the albedo of Earth, Incoming solar radiation flux $F_S = 1368\ \mathrm{Wm}^{-2}$. Emmisivity of earth as well as atmosphere is equal to 1.

To aid you further, consider a 'zoomed' view of the earth - atmosphere system shown in Figure 3. Think about all the unknown quantities in this figure. Form balance equations similar to part (A) involving these quantities and you shall have your answer !

*** SOLUTION ***

[5 points]. (A): Using the radiative equilibrium of the earth, we can write the following equation,

$$(1-\alpha)\, F_s \times \pi R_E^2 = \sigma T_E^4 \times 4\pi R_E^2 \ , \tag{3}$$

$$T_E = \sqrt[4]{\frac{(1-\alpha)\, F_s}{4\,\sigma}} \ , \tag{4}$$

where, α is the albedo of the earth, F_s in the incoming solar radiation, R_E and T_E is the radius and temperature of the earth respectively, and σ is the Stefan-Boltzmann constant. Inputting these values, which have been provided to the students, **The value of T_E is found to be 254.91 K**

[5 points]. (B): For this question, two equilibrium conditions need to be satisfied. One for the atmospheric layer and the one for earth. Let the temperature of the atmosphere and the earth be T_A and T_E respectively. Firstly, the budget of the atmosphere can be written as:

$$2 \times 4\pi R_E^2 \sigma T_A^4 = 4\pi R_E^2 \sigma T_E^4 \tag{5}$$

The factor of two on the L.H.S of the above equation is due to the fact that the atmosphere emits radiation from both it's inner and outer surface. On the other hand, the equation for earth can be written as:

$$4\pi R_E^2 \times \sigma T_E^4 = (1-\alpha)\, F_s \times \pi R_E^2 + 4\pi R_E^2 \sigma T_A^4 \tag{6}$$

Using Equation 5 to eliminate T_E from the above equation, we get the following result:

$$T_A = \sqrt[4]{\frac{(1-\alpha)\,F_s}{4\,\sigma}} \tag{7}$$

Thus, T_A is found to be equal to 254.91 K (Note that this is similar to the temperature of Earth in Part A). Once again using using Equation 5, but this time to solve for T_E , we get $T_E = \sqrt[4]{2} \times T_A$. **Thus,** $\mathbf{T_E = 303.14\,K}$.

QUESTION III

Choose the correct option from: (a,b,e,d,e,f). Each question below has a unique answer - Provide only the chosen option:

[3 points]. (A) Consider a pressure system in the **northern hemisphere** with isobars as shown in Figure 4. It is know that winds are in geostrophic balance. An imaginary parcel of air (denoted by a star in Figure 4) is released. What path would the star traverse ?

[3 points]. (B) Consider a similar pressure system as in Part (A) but that the atmosphere is initially kept at rest (using some magic). At time $t = 0$, the atmosphere is allowed to move. At the exact same instance, the imaginary parcel of air is released. What would be the path of the parcel in this case ?

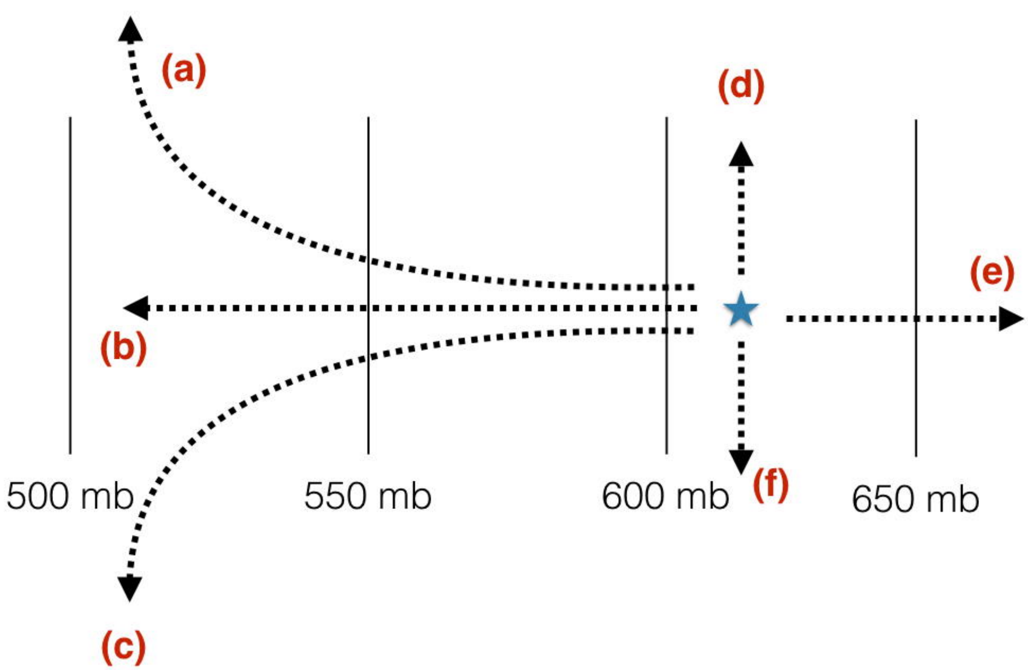

Figure 4: A pressure system in the northern hemisphere. How does the imaginary parcel of air denoted by a star move in cases (A) and (B) ?

*** SOLUTION ***

[3 points]. (A) **Choice (d)** , because the parcel will follow the geostrophic wind and go northward (given that we are in the northern hemisphere), parallel to the isobars

[3 points]. (B) **Choice (a)** , because initially the winds are at rest and when they are allowed to commence, they will follow the pressure gradient and move leftward. However, due to their velocity, the coriolis force will start acting and deflect the winds northward.

Question IV

Recall that the Leighton cycle is given by the following reactions:

$$\mathrm{NO_2} + h\nu \xrightarrow{j} \mathrm{NO} + \mathrm{O}$$

$$\mathrm{O} + \mathrm{O_2} \xrightarrow[k_1]{\mathrm{M}} \mathrm{O_3}$$

$$\mathrm{NO} + \mathrm{O_3} \xrightarrow{k_2} \mathrm{NO_2} + \mathrm{O_2}$$

[3 points]. (A) Under the photostationary state relationship, what is the expression that determines the $[\mathrm{NO_2}]/[\mathrm{NO}]$ ratio?

$$\frac{[\mathrm{NO_2}]}{[\mathrm{NO}]} = \frac{k_2}{j}[\mathrm{O_3}]$$

[10 points]. (B) Now, consider the additional reactions together with the ones above:

$$\mathrm{HO_2} + \mathrm{NO} \xrightarrow{k_3} \mathrm{OH} + \mathrm{NO_2}$$

$$\mathrm{RO_2} + \mathrm{NO} \xrightarrow{k_4} \mathrm{RO} + \mathrm{NO_2}$$

where R is an arbitrary hydrocarbon fragment. What is the new expression which determines the $[\mathrm{NO_2}]/[\mathrm{NO}]$ ratio under pseudo-steady-state assumption for $\mathrm{NO_2}$ and NO?

$$\frac{d[\mathrm{NO_2}]}{dt} = -j[\mathrm{NO_2}] + k_2[\mathrm{O_3}][\mathrm{NO}] + k_3[\mathrm{HO_2}][\mathrm{NO}] + k_4[\mathrm{RO_2}][\mathrm{NO}] \approx 0$$

$$\frac{[\mathrm{NO_2}]}{[\mathrm{NO}]} = \frac{1}{j}\left(k_2[\mathrm{O_3}] + k_3[\mathrm{HO_2}] + k_4[\mathrm{RO_2}]\right)$$

[2 points]. (C) Consider the previously-derived equation for ozone production efficiency (OPE):

$$OPE = \frac{k_{\mathrm{HO_2+NO}}[\mathrm{HO_2}][\mathrm{NO}]}{k_{\mathrm{OH+NO_2}}[\mathrm{OH}][\mathrm{NO_2}]}$$

Which of the relevant reactions above does this expression neglect to take into account?

$$RO_2 + NO \xrightarrow{k_4} RO + NO_2$$

Question V

Assume particles are spherical. For a population of aerosols with mass concentration m = 10 μg m^3, consider two scenarios: [1] the mass is distributed over a number of identical particles of diameter $D_{p,1}$ = 0.05 μm, and [2] the same mass is instead distributed over a fewer number of particles of diameter $D_{p,2}$ = 0.5 μm.

[10 points]. (A) Which population of particles has a longer condensation/evaporation timescale for achieving gas-particle equilibrium, and by how much? Use the Fuchs-Sutugin correction factor with mean free path of 0.118 μm, and a mass accommodation coefficient of one.

Scenario [2] is more rapid than scenario [1] by a factor of 474.

$$\begin{aligned}\frac{\tau_{s,2}}{\tau_{s,1}} &= \frac{D_{p,2}^2/f(2\lambda/D_{p,2},\alpha)}{D_{p,1}^2/f(2\lambda/D_{p,1},\alpha)} \\ &= \frac{0.5^2 \cdot 0.699}{0.05^2 \cdot 0.148} \\ &= 474\end{aligned}$$

[5 points]. (B) Provide a physical explanation for why the same mass concentration of particles distributed over different-sized particles leads to different timescales for condensation/evaporation.

Scenario [2] has a higher total surface area for mass transfer. The total surface area S for a given mass concentration (surface area to mass ratio) scales with R_p^{-1}.

$$\begin{aligned}m &= N\rho_p \frac{4}{3}\pi R_p^3 \\ m &= S \cdot \frac{1}{3}\rho_p R_p \quad \text{where} \quad S = N 4\pi R_p^2 \\ \frac{S}{m} &= \frac{3}{\rho_p R_p}\end{aligned}$$

Therefore, when distributed over smaller particles the mass transfer is more rapid.

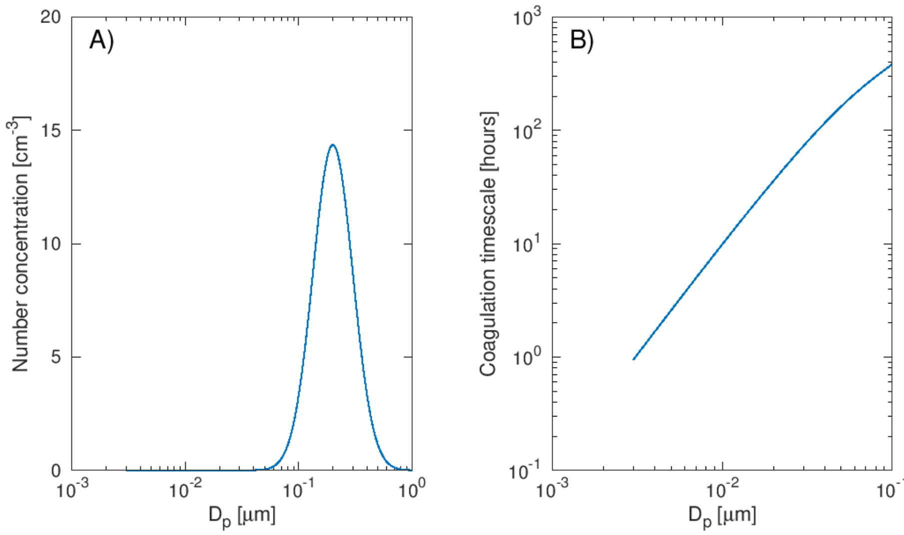

Figure 5: (A) Background particle concentration and (B) coagulation timescales.

Question VI

[5 points]. For a given a fixed background population of particles as shown in Figure 5A, the diameter-dependent coagulation timescale of particles with these background particles are shown in Figure 5B. Why does the characteristic timescale for coagulation decrease with particle size?

Coagulation rates of small particles with larger particles are more rapid than two large particles of similar size.

Question VII

Provide short answers to each of these questions (at most one sentence each):

[2 points]. (A) Which intermediate reactant is common to ozone formation in both the troposphere and stratosphere?

atomic oxygen

[2 points]. (B) What is the primary source of this intermediate reactant in the troposphere?

Photolysis of NO_2.

[2 points]. (C) What is the primary source of this intermediate reactant in the stratosphere?

Photolysis of O_3.

[4 points]. (D) Why are the answers for (B) and (C) not the same?

Photolysis of O_3 requires UV radiation but most is absorbed in the stratosphere; NO_2 can be photolyzed at wavelengths >250 nm.

Question VIII

[5 points]. Why is CFC-12 not effectively destroyed in the troposphere before reaching the stratosphere?

The major removal pathway for CFC-12 is photolysis, and its lifetime with respect to this loss is approximately 100 years.

Question IX

When estimating survival probabilities of newly-formed particles ($\sim$3 nm) to cloud condensation nuclei sizes ($\sim$100 nm), state reasons why these assumptions may not be valid under real atmospheric conditions:

[5 points]. (A) Fixed concentration gradient of condensing molecule.

Gas-phase pressure (p_∞) can be depleted, or the saturation vapor pressure (p_{eq}) of the particle can change. [*either answer accepted*]

[5 points]. (B) Fixed background particle concentration.

Growing particles would contribute to background population of particles onto which new particles can collide.