1) STRATOSPHERE-TROPOSPHERE EXCHANGE (Problem 3.3 in Jacob book)

The rate of exchange of air between the troposphere and the stratosphere is critical for determining the potential of various pollutants emitted from the surface to reach the stratosphere and affect the stratospheric ozone layer. One of the first estimates of this rate was made in the 1960s using measurements of strontium-90 (^{90}Sr) in the stratosphere. Strontium-90 is a radioactive isotope (half-life 28 years) produced in nuclear explosions. It has no natural sources. Large amounts of ^{90}Sr were injected into the stratosphere in the 1950s by above-ground nuclear tests. These tests were banned by international treaty in 1962. Following the test ban the stratospheric concentrations of ^{90}Sr began to decrease as ^{90}Sr was transferred to the troposphere. In the troposphere, ^{90}Sr is removed by wet deposition with a lifetime of 10 days (by contrast there is no rain, and hence no wet deposition, in the stratosphere). An intensive stratospheric measurement network was operated in the 1960s to monitor the decay of ^{90}Sr in the stratosphere. We interpret these observations here using a 2-box model for stratosphere-troposphere exchange with transfer rate constants k_{TS} and k_{ST} (yr^{-1}) between the tropospheric and stratospheric reservoirs. The reservoirs are assumed to be individually well-mixed.

Let M_S and M_T represent the masses of ^{90}Sr in the stratosphere and in the troposphere respectively. Observations of the decrease in the stratospheric inventory for the period 1963-1967 can be fitted to an exponential $M_S(t) = M_S(0)\exp(-kt)$ where $k = 0.77$ yr^{-1}.

1. Write mass balance equations for M_S and M_T in the 1963-1967 period.

2. Assuming that transfer of ^{90}Sr from the troposphere to the stratosphere is negligible (we will verify this assumption later), show that the residence time of air in the stratosphere is $\tau_S = 1/k_{ST} = 1.3$ years.

3. Let M'_T and M'_S represent the total masses of air in the troposphere and the stratosphere, respectively. Show that the residence time of air in the troposphere is $\tau_T = \tau_S (M'_T/M'_S) = 7.4$ years. Conclude as to the validity of your assumption in question 2.

4. Hydrochlorofluorocarbons (HCFCs) have been adopted as replacement products for the chlorofluorocarbons (CFCs), which were banned by the Montreal protocol because of their harmful effect on the ozone layer. In contrast to the CFCs, the HCFCs can be oxidized in the troposphere, and the oxidation products washed out by precipitation, so that most of the HCFCs do not penetrate into the stratosphere to destroy ozone. Two common HCFCs have trade names HCFC-123 and HCFC-124; their lifetimes against oxidation in the troposphere are 1.4 years and 5.9 years, respectively. There are no other sinks for these species in the troposphere. Using our 2-box model, determine what fractions of the emitted HCFC-123 and HCFC-124 penetrate the stratosphere.
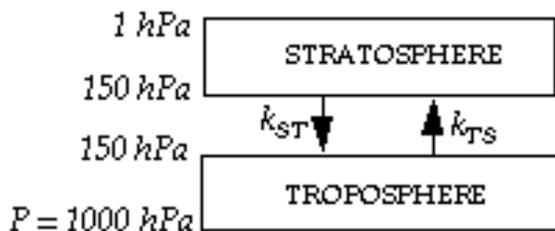
2) INTERHEMISPHERIC EXCHANGE (problem 3.4 in Jacob book)

In this problem we use observations of the radioactive gas ^{85}Kr to determine the characteristic time for exchange of air between the northern and southern hemispheres. We consider a 2-box model where each hemisphere is represented by a well-mixed box, with a rate constant k (yr^{-1}) for mass exchange between the two hemispheres. Our goal is to derive the residence time $\tau = 1/k$ of air in each hemisphere.

Krypton-85 is emitted to the atmosphere during the reprocessing of nuclear fuel. It is removed from the atmosphere solely by radioactive decay with a rate constant $k_c = 6.45\times10^{-2}$ yr^{-1}. The sources of ^{85}Kr are solely in the northern hemisphere and their magnitudes are well known due to regulation of the nuclear industry. Atmospheric concentrations of ^{85}Kr are fairly well known from ship observations. In 1983 the global ^{85}Kr emission rate was E = 15 kg yr^{-1}, the total atmospheric mass of ^{85}Kr in the northern hemisphere was M_N = 93 kg, and the total atmospheric mass of ^{85}Kr in the southern hemisphere was M_S = 86 kg.

1. Assume that the interhemispheric difference in the atmospheric mass of ^{85}Kr is at steady state, that is, $d(M_N - M_S)/dt = 0$ (we will justify this assumption in the next question). Express τ as a function of E, k_c, M_N, M_S and solve numerically using the 1983 values.

2. The global emission rate of ^{85}Kr was increasing during the 1980s at the rate of 3% yr^{-1}. Justify the assumption $d(M_N - M_S)/dt = 0$. [Hint: use the mass balance equation for $(M_N - M_S)$ to determine the time scale needed for $(M_N - M_S)$ to adjust to steady state following a perturbation.]

[To know more: Jacob, D. J., et al., Atmospheric distribution of ^{85}Kr simulated with a general circulation model, J. Geophys. Res., 92, 6614-6626, 1987.]

3) THE DETAILED CHAPMAN MECHANISM (Problem 10.3 in Jacob book)

We examine here some features of the detailed Chapman mechanism. Consider an air parcel at 44 km altitude, 30°N latitude, overhead Sun, $T = 263$ K, $n_a = 5.0 \times 10^{16}$ molecules cm^{-3}, and $[O_3] = 2.0 \times 10^{11}$ molecules cm^{-3}. The reactions involved in the mechanism are:

$$O_2 + h\nu \rightarrow 2O(^3P) \qquad k_1 = 6.0 \times 10^{-10} \text{ s}^{-1} \tag{1}$$

$$O_3 + h\nu \rightarrow O_2 + O(^3P) \qquad k_2 = 1.0 \times 10^{-3} \text{ s}^{-1} \tag{2}$$

$$O_3 + h\nu \rightarrow O_2 + O(^1D) \qquad k_3 = 4.1 \times 10^{-3} \text{ s}^{-1} \tag{3}$$

$$O(^3P) + O_2 + M \rightarrow O_3 + M \qquad k_4 = 6.0 \times 10^{-34} (T/300)^{-2.3} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1} \tag{4}$$

$$O(^1D) + N_2 \rightarrow O(^3P) + N_2 \qquad k_5 = 1.8 \times 10^{-11} \exp(110/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \tag{5}$$

$$O(^1D) + O_2 \rightarrow O(^3P) + O_2 \qquad k_6 = 3.2 \times 10^{-11} \exp(70/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \tag{6}$$

$$O(^3P) + O_3 \rightarrow 2O_2 \qquad k_7 = 8.0 \times 10^{-12} \exp(-2060/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \tag{7}$$
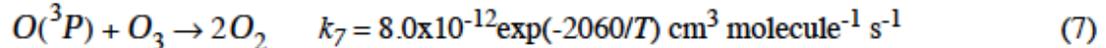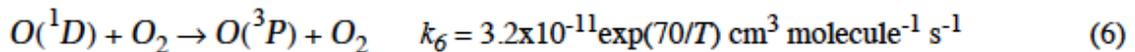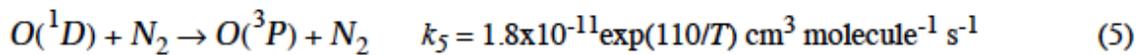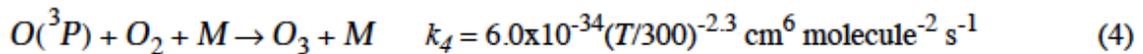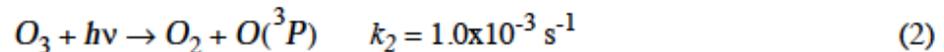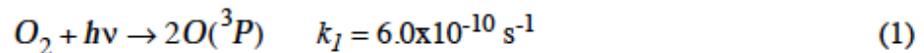
1. Assuming that reactions (1)-(7) are the only ones occurring in the air parcel:

1.1 Calculate the lifetime of $O(^1D)$ in the air parcel and its steady-state concentration.

1.2 Calculate the lifetime of $O(^3P)$ in the air parcel and its steady-state concentration.

1.3 Calculate the lifetime of O_x due to loss by the Chapman mechanism.

2. Assuming steady state for O_x, calculate the fraction of the total O_x sink in the air parcel that can actually be accounted for by the Chapman mechanism.