Solutions to Homework 2

1.

$$E = \frac{h \cdot c}{\lambda} \rightarrow \lambda = \frac{h \cdot c}{\Delta H_R}$$

$h = 1.58 \times 10^{-37}\, kcal \times s$, $c = 3 \times 10^{8}\, m/s$, $N_A = 6.02 \times 10^{23}\, molecule/mole$

For CFC-11, $\lambda_{\max} = \dfrac{1.58 \times 10^{-37}(kcal \times s) \times 3 \times 10^{8}(m/s)}{75.1(kcal/mol) / 6.02 \times 10^{23}(molecule/mole)} = 3.80 \times 10^{-7} m = 380 nm$

For CFC-12, $\lambda_{\max} = \dfrac{1.58 \times 10^{-37}(kcal \times s) \times 3 \times 10^{8}(m/s)}{79.5(kcal \times s) / 6.02 \times 10^{23}(molecule/mole)} = 3.59 \times 10^{-7} m = 359 nm$

2.

$$\tau = \frac{A}{F_i}$$

From the mixing ratio MR and the weight of the troposphere (M_T), the burden of the species is calculated:

$A = MR \cdot M_T \cdot \dfrac{MW}{MW_{air}}$ so, $\tau = MR \cdot M_T \cdot \dfrac{MW}{MW_{air}} \cdot \dfrac{1}{F_i}$

For CFC-11,

$$\tau = 0.268 \times 10^{-9} \times 4 \times 10^{21}(g) \times \frac{137.35(g/mole)}{28.9(g/mole)} \times \frac{1}{200(kt/year) \times 0.907 \times 10^{9}(g/kt)} = 28.0\, year$$

For CFC-12,

$$\tau = 0.503 \times 10^{-9} \times 4 \times 10^{21}(g) \times \frac{120.9(g/mole)}{28.9(g/mole)} \times \frac{1}{300(kt/year) \times 0.907 \times 10^{9}(g/kt)} = 28.1\, year$$

Because of their long lifetimes, CFC-11 and CFC-12 are well mixed horizontally and vertically in the troposphere.

3. Use the Arrhenius equation *k = A exp(-E$_a$/RT)* and the bimolecular lifetime τ =1/(*k*×[S])

	$S + O_3 \rightarrow SO + O_2$	$SO + O_3 \rightarrow SO_2 + O_2$	$SO_2 + O_3 \rightarrow SO_3 + O_2$
$\Delta H_R^0(298)$ $(kcal/mol)$	-99	-106.36	-57.74
$K(298)$ $cm^3/molecules \cdot s$	1.2×10^{-11}	8.98×10^{-14}	$< 1.88 \times 10^{-22}$
$\tau_{O3}(298)$ $(second)$	3.28	438.4	$> 2.09 \times 10^{11}$

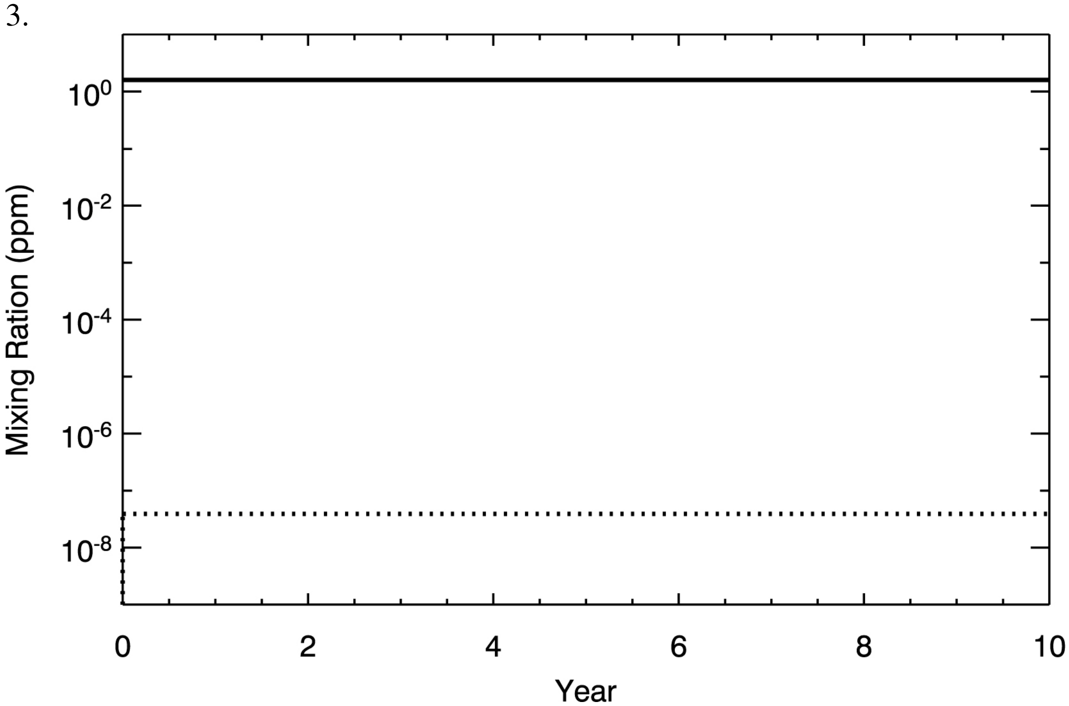
All the reaction enthalpies ΔH_R^0 are negative and are thermodynamically favorable in the atmosphere. From the lifetimes of O_3, S and SO are also efficient, but SO_2 is not efficient.

4.

1. $K(285) = A \cdot e^{-\frac{E_a}{RT}} = 2.45\times10^{-12} molecule/cm^3 \cdot s \times e^{-\frac{1775K}{285K}} = 4.83\times10^{-15} cm^3/molecule \cdot s$

2. $\tau = \frac{1}{K(285)\cdot[OH]} = \frac{1}{4.83\times10^{-15}(cm^3/molecule\cdot s)\times10^6(molecule/cm^3)} = 6.56\,year$

3.



The solid and dots lines correspond to the CH_4 H_2O mixing ratios, respectively.