Problem Set 1: 5 February 2014 Due: 12 February 2014

Press (hPa)	Temp (K)	J_{O2} (sec-1)	$J_{O3\text{-->}O1D}$ (sec-1)	$J_{O3\text{-->}O3P}$ (sec-1)	[M] cm^{-3}	$[O_2]$ cm^{-3}	$[O_3]$ cm^{-3}	[O] cm^{-3}	$[O]/[O_3]$	f_{O3} (ppmv)
100	194	1.0e-13	3.6e-5	4.6e-4						
52	212	8.7e-13	3.5e-5	4.6e-4						
31	218	3.7e-12	4.5e-5	4.6e-4						
18	223	1.9e-11	7.5e-5	4.7e-4						
10	227	6.8e-11	1.5e-4	4.9e-4						
5.6	232	2.3e-10	3.4e-4	5.2e-4						
2.4	251	7.1e-10	1.4e-3	6.6e-4						
0.9	255	1.5e-9	4.0e-3	9.6e-4						

At each pressure, what is the total density [M]? What is the O_2 density $[O_2]$?

Assuming only the Chapman mechanism of pure oxygen reactions, hat is the ozone density $[O_3]$? What is the atomic oxygen density [O]? What is the ratio $[O]/[O_3]$? What is the ozone mixing ratio, f_{03}?

Two-body reactions: $k(T) = A \cdot e^{-\frac{E}{R}/T}$

Reaction	A-Factor	E/R	k(298K)
$O + O_3 \rightarrow O_2 + O_2$	8.0×10^{-12}	2060	8.0×10^{-15}
$O + NO_2 \rightarrow NO + O_2$	6.5×10^{-12}	-120	9.7×10^{-12}
$O_3 + NO \rightarrow NO_2 + O_2$	2.0×10^{-12}	1400	1.8×10^{-14}
$O + HO_2 \rightarrow OH + O_2$	3.0×10^{-11}	-200	5.9×10^{-11}
$O + OH \rightarrow H + O_2$	2.2×10^{-11}	-120	3.3×10^{-11}
$O_3 + HO_2 \rightarrow OH + O_2 + O_2$	1.1×10^{-14}	500	2.0×10^{-15}
$O_3 + OH \rightarrow HO_2 + O_2$	1.6×10^{-12}	940	6.8×10^{-14}
$Cl + O_3 \rightarrow ClO + O_2$	2.9×10^{-11}	260	1.2×10^{-11}
$ClO + O \rightarrow Cl + O_2$	3.0×10^{-11}	-70	3.8×10^{-11}
$Br + O_3 \rightarrow BrO + O_2$	1.7×10^{-11}	800	1.2×10^{-12}
$BrO + ClO \rightarrow Br + Cl + O_2$	2.9×10^{-12}	-220	6.1×10^{-12}
$BrO + BrO \rightarrow Br + Br + O_2$	1.4×10^{-12}	-150	2.3×10^{-12}
$Cl + CH_4 \rightarrow HCl + CH_3$	1.1×10^{-11}	1400	1.0×10^{-13}
$OH + HCl \rightarrow H_2O + Cl$	2.6×10^{-12}	350	8.0×10^{-13}

Three-body reactions: $LowPressureLimit \quad k_o(T) = k_o^{300} \cdot \left(\frac{T}{300}\right)^{-n}$

Reaction	k_o^{300}	n	k_∞^{300}	m
$O + O_2 + M \rightarrow O_3 + M$	6.0×10^{-34}	2.3	-	-
$OH + NO_2 + M \rightarrow HNO_3 + M$	2.6×10^{-30}	3.2	2.4×10^{-11}	1.3
$H + O_2 + M \rightarrow HO_2 + M$	5.7×10^{-32}	1.6	7.5×10^{-11}	0
$ClO + NO_2 + M \rightarrow ClONO_2 + M$	1.8×10^{-31}	3.4	1.5×10^{-11}	1.9

At each pressure level, what is the time constant for conversion of NO to NO_2? If J_{NO2} =1.e-2, what is the fraction of cycles of NO to NO_2 and back that lead to catalysis by reaction with atomic oxygen? What is the ratio of NO to NO_2 at each pressure level?

What would the NO_x concentration ($[NO_x]=[NO]+[NO_2]$) have to be to make the ozone loss due to this cycle equal to that of the pure oxygen chain termination step $O + O_3 \rightarrow O_2 + O_2$?