Group Names _KEY___

Stratospheric Chemistry Problem:
1. By carrying out a number of calculations or thought experiments, we can better understand the Chapman Mechanism chemistry involving ozone production and destruction.

The Chapman mechanism reactions are:
1) \( \text{O}_2 + \text{h}_\nu \rightarrow 2\text{O} \)
2) \( \text{O} + \text{O}_2 + \text{M} \rightarrow \text{O}_3 + \text{M} \)
3) \( \text{O}_3 + \text{h}_\nu \rightarrow \text{O}_2 + \text{O} \)
and 4) \( \text{O} + \text{O}_3 \rightarrow 2\text{O}_2 \)

Additional Needed information: \( N_{\text{AvA}} = 6.02 \times 10^{23} \) molec/mol and assume that >99% of O in stratosphere is in form \( \text{O}_2 \). [put on board]

Answer the following specific questions:
1. What does M refer to in step 2)? any air molecule (just to remove extra kinetic energy)

2. If the rate constant, \( k \), for reaction 2 is \( 2 \times 10^{-33} \) cm\(^6\) molec\(^{-2}\) s\(^{-1}\), calculate the lifetime of O atoms with respect to loss by reaction 2 at 25 km if \( P_{\text{air}} = 0.04 \) atm and %O\(_2\) by volume = 20%. Assume \( T = -40^\circ\text{C} \). \( R = 0.0821 \) L atm/mol K and 0°C = 273 K.
Hint: you can use the ideal gas law to get \( n/V \) in mol/L and then convert to molec cm\(^{-3}\). The lifetime (in s) can be calculated as the ratio of the concentration (molec cm\(^{-3}\)) to the sink (molec O cm\(^{-3}\) s\(^{-1}\)), cancelling out [O] (since it is not given).

\[
\tau = \left[ \frac{\text{O}}{ \frac{d[\text{O}]}{dt} } \right] = \frac{\left[ \text{O} \right]}{\left[ k[\text{O}] [\text{O}_2] [\text{M}] \right]} = \frac{1}{k[\text{O}_2] [\text{M}]}
\]

\[
[M] = \frac{n}{V} = \frac{P_{\text{air}}}{RT} = \frac{0.04 \text{ atm}}{[\left(0.0821 \text{ L atm/mol K}(273 - 400K)\right)]} = 0.04 \text{ atm/}(19.1 \text{ L atm/mol K})
\]

\[
[M] = (0.00209 \text{ mol/L})(6.02 \times 10^{23} \text{ molec/mol})(1\text{L}/1000 \text{ cm}^3) = 1.26 \times 10^{18} \text{ molec/cm}^3
\]

\[
[O_2] = 0.2[M] = 2.52 \times 10^{17} \text{ molec/cm}^3
\]

\[
\tau = \frac{1}{[\left(2 \times 10^{-33} \text{ cm}^6 \text{ molec}^{-2} \text{ s}^{-1}\right)(1.26 \times 10^{18} \text{ molec/cm}^3)(2.52 \times 10^{17} \text{ molec/cm}^3)]} = 0.0002 \text{ s}
\]

3. Within the stratosphere, how will the lifetime of O with respect to reaction 2 depend on altitude?
It will decrease because [M] and [O\(_2\)] decrease with altitude due to the decrease in P.

4. At night in the stratosphere, reactions 1 and 3 are stopped. Would you expect the concentration of O\(_3\) to decrease to zero? What about the concentration of O atoms? You can assume that the concentration of O\(_3\) is much higher than O atoms.
Sources of both O\(_3\) and O are stopped at night. Because reaction 2 is fast, O atoms will quickly be depleted and go to zero concentration. Once O atoms are gone, reaction 4 can’t proceed and the ozone concentration will be constant (no source and no sink).