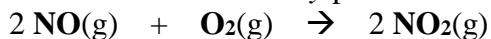


Example Questions involving Gas Phase Kinetics

1. Trichloroethylene (TCE) is an example of a volatile organic compound. Its bimolecular reaction with **OH** has $k = 2.3 \times 10^{-12} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ at 300 K. Estimate the *half-life* and *residence time* (lifetime) of TCE in the atmosphere if the average concentration of **OH** remains fairly constant at $2.0 \times 10^6 \text{ molec cm}^3$.

[Ans: $t_{1/2}(\text{TCE}) = 42 \text{ hr}$; $\tau(\text{TCE}) = 60 \text{ hr}$]

2. Assume the following reaction is an *elementary* process.



- Write the rate law for this reaction.
- A sample of air at 290 K is contaminated by 1.0 ppm_v of **NO**. Under these conditions, can the rate law be simplified?
- Under the conditions described in b), the half-life of **NO** has been estimated at 100 hrs. What would the half-life be if the initial **NO** concentration were 12 ppm_v?

[Ans: a) $\text{rate} = k [\text{NO}]^2 [\text{O}_2]$
b) $\text{rate} = k' [\text{NO}]^2$, where $k' = k [\text{O}_2]$ is a pseudo second order rate constant
c) $t_{1/2}(\text{NO}) = 8.3 \text{ hr}$]

3. The reaction



has a rate constant = $1.1 \times 10^{-33} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$ at 220K (stratosphere).

a) What is the rate of reaction if $P_T = 0.010 \text{ atm}$ and the concentration of atomic oxygen is $2.1 \times 10^{-4} \text{ ppm}_v$.

b) Calculate the *pseudo*-first order rate constant for this reaction and the *lifetime* (i.e., residence time) for of $\text{O}(\text{g})$ under these conditions.

[Ans: a) rate = $1.8 \times 10^9 \text{ molec cm}^{-3} \text{ s}^{-1}$
b) $k' = k [\text{O}_2] [\text{M}] = 25.7 \text{ s}^{-1}$; $\tau(\text{O}) = 39 \text{ ms}$]

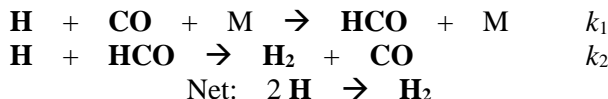
4. What is the *lifetime* (i.e., residence time) of atomic oxygen in the troposphere if its major sink is the reaction



Assume 15°C , 1.00 atm and that $k = 6.0 \times 10^{-34} (\text{T}/300)^{-2.3} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$? Compare this result with that found in Q3, above.

[Ans: $\tau(\text{O}) = 11 \mu\text{s}$; Note that atomic O is much shorter lived in the troposphere than the stratosphere due to the much greater number densities of at higher pressures.]

5. A catalytic cycle that might have contributed to the formation of H_2 from H in the early atmosphere of the Earth is



Calculate the *steady state* concentration of the radical HCO , if the concentrations of CO and M were 1.0×10^{12} and $2.5 \times 10^{19} \text{ molecules cm}^{-3}$, respectively and the magnitudes of the rate constants k_1 and k_2 are $1.0 \times 10^{-34} \text{ cm}^6 \text{ molecules}^{-2} \text{ s}^{-1}$ and $3.0 \times 10^{-10} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$, respectively.

[Ans: $[\text{HCO}] = 8.3 \times 10^6 \text{ molec/cm}^3$]