

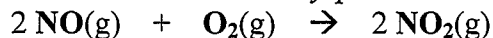
Example Questions involving Gas Phase Kinetics

1. Trichloroethylene (TCE) is an example of a volatile organic compound. Its bimolecular ~~rate~~ 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 $2.0 \times 10^6 \text{ molec cm}^{-3}$.

$$\begin{aligned} \text{rate} &= k [\text{TCE}] [\text{OH}] \\ \text{if } [\text{OH}] \text{ is constant, then } \text{rate} &= k' [\text{TCE}] \text{ (pseudo 1st order)} \\ \text{where } k' &= k [\text{OH}] \\ &= \left(2.3 \times 10^{-12} \frac{\text{cm}^3}{\text{molec} \cdot \text{s}} \right) \left(2.0 \times 10^6 \frac{\text{molec}}{\text{cm}^3} \right) \\ &= 4.6 \times 10^{-6} \text{ s}^{-1} \\ t_{1/2} &= \frac{0.693}{k'} = \frac{0.693}{4.6 \times 10^{-6} \text{ s}^{-1}} = 1.51 \times 10^5 \text{ s} = 42 \text{ hr} \\ \tau &= \frac{1}{k'} = \frac{1}{4.6 \times 10^{-6} \text{ s}^{-1}} = 2.17 \times 10^5 \text{ s} = 60 \text{ hr} \end{aligned}$$

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

2. Assume the following reaction is an elementary process.

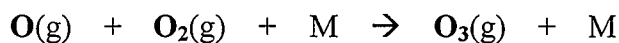


- Write the rate law for this reaction.
- A sample of air at 290 K is contaminated by 1.0 ppm_v of NO. Under these conditions, can the rate law be simplified?
- Under the conditions described in b), the half-life of NO has been estimated at 100 hrs. What would the half-life be if the initial NO concentration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

$$\begin{aligned} \text{a) } \text{rate} &= k [\text{NO}]^2 [\text{O}_2] \quad \text{third order overall} \\ \text{b) } \text{Conc. of } \text{O}_2 &= 210,000 \text{ ppm}_v \gg \text{Conc. of NO} = 1.0 \text{ ppm}_v \\ \therefore \text{rate} &= k' [\text{NO}]^2 \text{ (pseudo 2nd order)} \\ \text{where } k' &= k [\text{O}_2] \\ \text{c) } \text{when Conc. NO} &= 1.0 \text{ ppm}_v, t_{1/2} = 100 \text{ hr} \\ t_{1/2} &= \frac{1}{[A]_0 k'} \quad \therefore k' = \frac{1}{[A]_0 t_{1/2}} = \frac{1}{1.0 \text{ ppm}_v \cdot 100 \text{ hr}} = 1.0 \times 10^{-2} \text{ ppm}_v^{-1} \text{ hr}^{-1} \\ \text{if Conc. NO} &= 12 \text{ ppm}_v \\ t_{1/2} &= \frac{1}{(12 \text{ ppm}_v)(1.0 \times 10^{-2} \text{ ppm}_v^{-1} \text{ hr}^{-1})} = \frac{1}{0.12 \text{ hr}^{-1}} = 8.3 \text{ hr} \end{aligned}$$

[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) $t_{1/2} = 8.3 \text{ hr}$]

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 (residence time) for of $\text{O}(\text{g})$ under these conditions.

$$\text{rate} = k [\text{O}][\text{O}_2][\text{M}]$$

$$\begin{aligned} [\text{M}] &= n_{\text{air}}^* = \frac{P}{RT} \cdot N_A \cdot \frac{1 \text{ L}}{10^3 \text{ cm}^3} \\ &= \frac{(0.010 \text{ atm}) (6.023 \times 10^{23}) 1 \text{ L}}{(0.08206 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}}) (220 \text{ K}) 10^3 \text{ cm}^3} \\ &= 3.34 \times 10^{17} \frac{\text{molec}}{\text{cm}^3} \end{aligned}$$

$$\begin{aligned} [\text{O}_2] &= n_{\text{O}_2}^* = \chi_{\text{O}_2} n_{\text{air}}^* \\ &= 0.21 (3.34 \times 10^{17} \frac{\text{molec}}{\text{cm}^3}) = 7.01 \times 10^{16} \frac{\text{molec}}{\text{cm}^3} \end{aligned}$$

$$\begin{aligned} [\text{O}] &= n_{\text{O}}^* = \chi_{\text{O}} n_{\text{air}}^* \\ &= \frac{0.00021}{10^6} (3.34 \times 10^{17} \frac{\text{molec}}{\text{cm}^3}) = 7.01 \times 10^7 \frac{\text{molec}}{\text{cm}^3} \end{aligned}$$

$$\begin{aligned} \text{a) rate} &= \left(1.1 \times 10^{-33} \frac{\text{cm}^6}{\text{molec}^2 \text{ s}} \right) (3.34 \times 10^{17} \frac{\text{molec}}{\text{cm}^3}) (7.01 \times 10^{16} \frac{\text{molec}}{\text{cm}^3}) (7.01 \times 10^7 \frac{\text{molec}}{\text{cm}^3}) \\ &= 1.8 \times 10^9 \frac{\text{molec}}{\text{cm}^3 \text{ s}} \end{aligned}$$

$$\begin{aligned} \text{b) } k' &= k [\text{O}_2][\text{M}] \\ &= \left(1.1 \times 10^{-33} \frac{\text{cm}^6}{\text{molec} \cdot \text{s}} \right) (7.01 \times 10^{16} \frac{\text{molec}}{\text{cm}^3}) (3.34 \times 10^{17} \frac{\text{molec}}{\text{cm}^3}) \\ &= 25.8 \text{ s}^{-1} \end{aligned}$$

$$\tau = \frac{1}{k'} = 0.0388 \text{ s} = 39 \text{ ms}$$

[Ans: a) rate = $1.8 \times 10^9 \text{ molec cm}^{-3} \text{ s}^{-1}$
b) $k' = k [\text{O}_2][\text{M}] = 25.7 \text{ s}^{-1}$ ($t_{1/2} = 27 \text{ ms}$)

$$\tau = \frac{1}{k'} = 39 \text{ ms}$$

4. What is the lifetime (ie, 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.

$\tau = \frac{1}{k'}$ where k' is pseudo 1st order rate constant

rate = $k'[\text{O}]$ if $[\text{O}_2] \neq [\text{M}] \gg [\text{O}]$

where $k' = k[\text{O}_2][\text{M}]$

$$[\text{M}] = n_{\text{air}}^* = \frac{P}{RT} \cdot N_A \cdot \frac{1 \text{ L}}{10^3 \text{ cm}^3} = 2.55 \times 10^{19} \frac{\text{molec}}{\text{cm}^3}$$

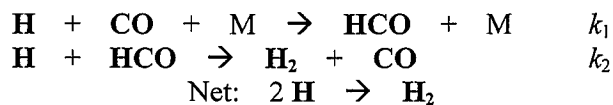
$$\begin{aligned} [\text{O}_2] &= n_{\text{O}_2}^* = 0.21 \left(2.55 \times 10^{19} \frac{\text{molec}}{\text{cm}^3} \right) \\ &= 5.35 \times 10^{18} \frac{\text{molec}}{\text{cm}^3} \end{aligned}$$

$$\begin{aligned} \therefore k' &= \left[6.0 \times 10^{-34} \left(\frac{288}{300} \right)^{-2.3} \frac{\text{cm}^6}{\text{molec} \cdot \text{s}} \right] \left(2.55 \times 10^{19} \frac{\text{molec}}{\text{cm}^3} \right) \\ &\quad \times \left(5.35 \times 10^{18} \frac{\text{molec}}{\text{cm}^3} \right) = 8.99 \times 10^4 \text{ s}^{-1} \end{aligned}$$

$$\therefore \tau = \frac{1}{k'} = 1.1 \times 10^{-5} \text{ s} = 11 \mu\text{s}$$

[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 2.5×10^{19} molecules cm^{-3} , respectively and the magnitudes of the rate constants k_1 and k_2 are 1.0×10^{-34} $\text{cm}^6 \text{molecules}^{-2} \text{s}^{-1}$ and 3.0×10^{-10} $\text{cm}^3 \text{molecules}^{-1} \text{s}^{-1}$, respectively.

At steady state, $\frac{d[\text{HCO}]}{dt} = 0$

$$\frac{d[\text{HCO}]}{dt} = \underbrace{k_1 [\text{H}][\text{CO}][\text{M}]}_{\text{produced in step 1}} - \underbrace{k_2 [\text{H}][\text{HCO}]}_{\text{reacted by step 2}} = 0$$

$$\therefore k_1 [\text{H}][\text{CO}][\text{M}] = k_2 [\text{H}][\text{HCO}]$$

$$\text{So } [\text{HCO}] = \frac{k_1}{k_2} [\text{CO}][\text{M}]$$

$$= \frac{\left(1.0 \times 10^{-34} \frac{\text{cm}^6}{\text{molec}^2 \text{s}}\right)}{\left(3.0 \times 10^{-10} \frac{\text{cm}^3}{\text{molec s}}\right)} \left(1.0 \times 10^{12} \frac{\text{molec}}{\text{cm}^3}\right) \left(2.5 \times 10^{19} \frac{\text{molec}}{\text{cm}^3}\right)$$

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

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