Example Questions involving Gas Phase Kinetics

1. Trichloroethylene (TCE) is an example of a volatile organic compound. Its bimolecular reaction with **OH** has $k = 2.3 \times 10^{-12}$ cm^3 molec^{-1} 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 2.0×10^6 molec cm^3.

rate = k[TCE][OH]

if [OH] is constant, then rate = k'[TCE] (pseudo 1st order)

where $k' = k$[OH]

$$= \left(2.3\times10^{-12}\ \frac{cm^3}{molec \cdot s}\right)\left(2.0\times10^{6}\ \frac{molec}{cm^3}\right)$$

$$= 4.6\times10^{-6}\ s^{-1}$$

$$t_{1/2} = \frac{0.693}{k'} = 1.51\times10^{5}\ s = 42\ hr \qquad \tau = \frac{1}{k'} = 2.17\times10^{5}\ s = 60\ hr$$

[*Ans:* $t_{1/2}$ *(TCE) = 42 hr;* τ*(TCE) = 60 hr*]

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

$$2\,NO(g) + O_2(g) \rightarrow 2\,NO_2(g)$$

a) Write the rate law for this reaction.

b) 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?

c) 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$_v$?

a) rate = $k[NO]^2[O_2]$ third order overall

b) Conc. of O_2 = 210,000 ppm$_v$ >> Conc. of NO = 1.0 ppm$_v$

∴ rate = $k'[NO]^2$ (pseudo 2nd order)

where $k' = k[O_2]$

c) when Conc. NO = 1.0 ppm, $t_{1/2}$ = 100. hr

$$t_{1/2} = \frac{1}{[A]_0 k'} \quad \therefore \quad k' = \frac{1}{[A]_0 t_{1/2}} = \frac{1}{1.0\ ppm_v \cdot 100\ hr} = 1.0\times10^{-2}\ ppm_v^{-1}\ hr^{-1}$$

if Conc. NO = 12 ppm$_v$

$$t_{1/2} = \frac{1}{(12\ ppm_v)(1.0\times10^{-2}\ ppm_v^{-1}\ hr^{-1})} = \frac{1}{0.12\ hr^{-1}} = 8.3\ hr$$

[*Ans:* *a) rate = k* $[\mathbf{NO}]^2[\mathbf{O_2}]$

b) rate = k' $[\mathbf{NO}]^2$*, where k' = k* $[\mathbf{O_2}]$ *is a pseudo second order rate constant*

c) $t_{1/2}$ *= 8.3 hr]*

3. The reaction

$$O(g) + O_2(g) + M \rightarrow O_3(g) + M$$

has a rate constant = 1.1×10^{-33} cm^6 $molecule^{-2}$ s^{-1} at 220K (stratosphere).
a) What is the rate of reaction if P_T = 0.010 atm and the concentration of atomic oxygen is 2.1×10^{-4} ppm_v.
b) Calculate the *pseudo*-first order rate constant for this reaction and the lifetime (residence time) for of **O**(g) under these conditions.

$$rate = k[O][O_2][M]$$

$$[M] = n^*_{air} = \frac{P}{RT} \cdot N_A \cdot \frac{1\,L}{10^3\,cm^3}$$

$$= \frac{(0.010\ atm)(6.023 \times 10^{23})\ 1L}{(0.08206\ \frac{L \cdot atm}{mol \cdot K})(220\ K)\ 10^3\,cm^3}$$

$$= 3.34 \times 10^{17}\ \frac{molec}{cm^3}$$

$$[O_2] = n^*_{O_2} = X_{O_2}\, n^*_{air}$$

$$= 0.21\left(3.34 \times 10^{17}\ \frac{molec}{cm^3}\right) = 7.01 \times 10^{16}\ \frac{molec}{cm^3}$$

$$[O] = n^*_O = X_O\, n^*_{air}$$

$$= \frac{0.00021}{10^6}\left(3.34 \times 10^{17}\ \frac{molec}{cm^3}\right) = 7.01 \times 10^{7}\ \frac{molec}{cm^3}$$

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

$$= 1.8 \times 10^{9}\ \frac{molec}{cm^3\ s}$$

b) $$k' = k[O_2][M]$$

$$= \left(1.1 \times 10^{-33}\ \frac{cm^6}{molec \cdot s}\right)\left(7.01 \times 10^{16}\ \frac{molec}{cm^3}\right)\left(3.34 \times 10^{17}\ \frac{molec}{cm^3}\right)$$

$$= 25.8\ s^{-1}$$

$$\tau = 1/k' = 0.0388\ s = 39\ ms$$

[*Ans:* *a) rate =* 1.8×10^9 *molec* $cm^{-3}\ s^{-1}$
b) $k' = k\,[O_2]\,[M] = 25.7\ s^{-1}$; ($t_{1/2} = 27\ ms$)]

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

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

$$\mathbf{O}(g) \; + \; \mathbf{O_2}(g) \; + \; M \rightarrow \mathbf{O_3}(g) \; + \; M$$

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

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

rate $= k'[O]$ if $[O_2]$ & $[M] \gg [O]$

where $k' = k[O_2][M]$

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

$$[O_2] = n^*_{O_2} = 0.21\left(2.55 \times 10^{19}\ \frac{molec}{cm^3}\right)$$

$$= 5.35 \times 10^{18}\ \frac{molec}{cm^3}$$

$$\therefore k' = \left[6.0 \times 10^{-34}\left(\frac{288}{300}\right)^{-2.3} \frac{cm^6}{molec \cdot s}\right]\left(2.55 \times 10^{19}\ \frac{molec}{cm^3}\right)$$

$$\times \left(5.35 \times 10^{18}\ \frac{molec}{cm^3}\right) = 8.99 \times 10^4\ s^{-1}$$

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

[*Ans: τ (**O**) = 11 μs; 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 $\mathbf{H_2}$ from **H** in the early atmosphere of the Earth is

$$\mathbf{H} + \mathbf{CO} + \mathrm{M} \rightarrow \mathbf{HCO} + \mathrm{M} \qquad k_1$$
$$\mathbf{H} + \mathbf{HCO} \rightarrow \mathbf{H_2} + \mathbf{CO} \qquad k_2$$
$$\text{Net: } 2\,\mathbf{H} \rightarrow \mathbf{H_2}$$

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} cm^6 molecules^{-2} s^{-1} and 3.0×10^{-10} cm^3 molecules^{-1} s^{-1}, respectively.

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

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

$$\therefore \; k_1 [H][CO][M] = k_2 [H][HCO]$$

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

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

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

[*Ans: [**HCO**] = 8.3 x 10^{6} molec/cm^{3}*]