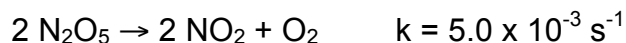


## Conference #3 – Solutions

$$\ln[A]_t = \ln[A]_o - k t \quad 1/[A]_t = 1/[A]_o + k t \quad \tau = [A]/\text{rate of removal of A}$$

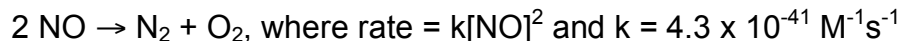
1.  $\text{N}_2\text{O}_5$  decays in a first order process as follows:



How long will it take for the concentration of  $\text{N}_2\text{O}_5$  to drop from 0.050 M to 0.010 M?

$$\begin{aligned} \ln(0.010) &= \ln(0.050) - 2(0.0050 \text{ s}^{-1})t \\ t &= -[\ln(0.01/0.05)]/(0.010 \text{ s}^{-1}) = \mathbf{160 \text{ s}} \end{aligned}$$

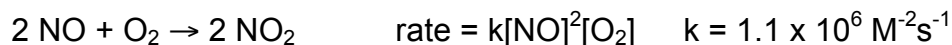
2. NO reacts by itself in a second order process:



- a. What would be the half-life of NO given an initial concentration of  $4.1 \times 10^{-9} \text{ M}$ ?

$$\begin{aligned} t_{1/2} &= 1/(2k[\text{NO}]_o) \\ &= 1/(2 \cdot 4.3 \times 10^{-41} \text{ M}^{-1}\text{s}^{-1})(4.1 \times 10^{-9} \text{ M}) \\ &= 2.8 \times 10^{48} \text{ s} = 5.4 \times 10^{42} \text{ years. not soon.} \end{aligned}$$

- b. NO reacts more rapidly with  $\text{O}_2$  as follows:



Given  $[\text{O}_2]$  at sea level is 0.0086 M, what is the lifetime of NO in the atmosphere?

Given how slow that first reaction is (part a) we can just use the second rxn.

$$\tau = 1/k[\text{NO}][\text{O}_2] = 1/(1.1 \times 10^6 \text{ M}^{-1}\text{s}^{-1})(0.0086 \text{ M})(4.1 \times 10^{-9} \text{ M}) = 2.6 \times 10^4 \text{ s (7 hr)}$$

3. Consider the following reaction mechanism



a. Write the balanced reaction for this process, identifying reactants, products, intermediates and catalysts.

Reactants =  $O_3$  &  $O$

Products =  $O_2$

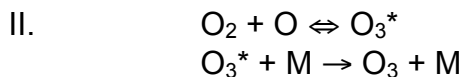
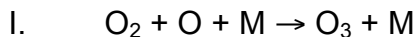
Catalyst =  $HO$

Int =  $HO_2$

b. What are the rate laws for each of these two steps?

see above

4. Compare two mechanisms for the reaction of  $O_2$  with  $O$  to form ozone:



a. What is the rate law predicted for the first mechanism?

$$\text{rate} = k[O_2][O][M]$$

b. What is the rate law predicted for the second mechanism if the first step is slow?

$$\text{rate} = k[O_2][O]$$

c. What is the rate law predicted for the second mechanism if the second step is slow, and the rapid equilibrium assumption is applied to the first step?

$$\text{rate} = k_2[O_3^*][M] \quad \text{but we need to replace } [O_3^*]$$

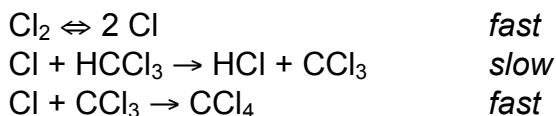
$$k_1[O_2][O] = k_{-1}[O_3^*], \text{ which means: } [O_3^*] = (k_1/k_{-1})[O_2][O]$$

now substitute into the above...

$$\text{rate} = k_2(k_1/k_{-1})[O_2][O][M]$$

5. For the reaction:  $Cl_2 + HCCl_3 \rightarrow HCl + CCl_4$   
we get the unusual experimental result:  $\text{rate} = k[HCCl_3][Cl_2]^{1/2}$

Show that this mechanism is consistent with the exp. rate law:



rate of slow step =  $k_2[Cl][HCCl_3]$  but  $Cl$  is an intermediate...

$$k_1[Cl_2] = k_{-1}[Cl]^2$$

$[Cl] = \{(k_1/k_{-1})[Cl_2]\}^{1/2}$  substituting into rate law for 2<sup>nd</sup> step we get:

$$\text{rate} = k_2\{(k_1/k_{-1})[Cl_2]\}^{1/2}[HCCl_3] = k[Cl_2]^{1/2}[HCCl_3]$$

$$\text{where } k = k_2(k_1/k_{-1})^{1/2}$$