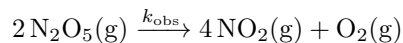


## 4 Mechanisms II / Gas-Phase Reactions

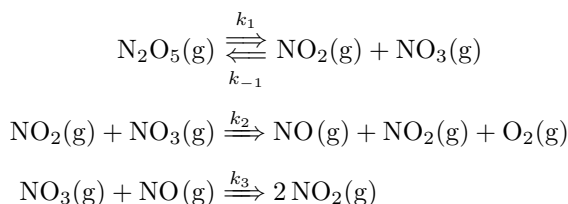
### Chapter 29

From McQuarrie and Simon (1997).

5/9: **29-11.** Consider the decomposition reaction of  $\text{N}_2\text{O}_5(\text{g})$



A proposed mechanism for this reaction is

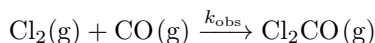


Assume that the steady-state approximation applies to both the  $\text{NO}(\text{g})$  and  $\text{NO}_3(\text{g})$  reaction intermediates to show that this mechanism is consistent with the experimentally observed rate law

$$\frac{d[\text{O}_2]}{dt} = k_{\text{obs}}[\text{N}_2\text{O}_5]$$

Express  $k_{\text{obs}}$  in terms of the rate constants for the individual steps of the reaction mechanism.

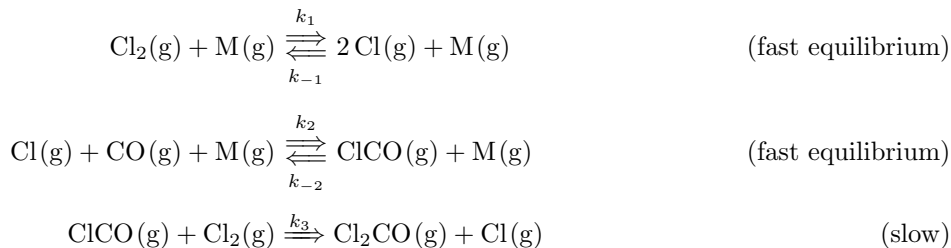
**29-12.** The rate law for the reaction



between  $\text{CO}(\text{g})$  and  $\text{Cl}_2(\text{g})$  to form phosgene ( $\text{Cl}_2\text{CO}$ ) is

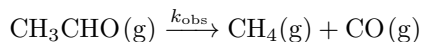
$$\frac{d[\text{Cl}_2\text{CO}]}{dt} = k_{\text{obs}}[\text{Cl}_2]^{3/2}[\text{CO}]$$

Show that the following mechanism is consistent with this rate law.

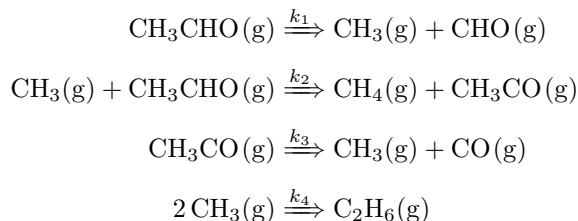


where M is any gas molecule present in the reaction container. Express  $k_{\text{obs}}$  in terms of the rate constants for the individual steps of the reaction mechanism.

**29-28.** Consider the mechanism for the thermal decomposition of acetaldehyde



given as follows.

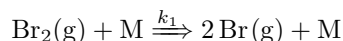


Show that  $E_{\text{obs}}$ , the measured Arrhenius activation energy for the overall reaction, is given by

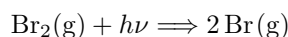
$$E_{\text{obs}} = E_2 + \frac{1}{2}(E_1 - E_4)$$

where  $E_i$  is the activation energy of the  $i^{\text{th}}$  step of the reaction mechanism. How is  $A_{\text{obs}}$ , the measured Arrhenius pre-exponential factor for the overall reaction, related to the Arrhenius pre-exponential factors for the individual steps of the reaction mechanism?

- 29-33.** It is possible to initiate chain reactions using photochemical reactions. For example, in place of the thermal initiation reaction for the  $\text{Br}_2(\text{g}) + \text{H}_2(\text{g})$  chain reaction



we could have the photochemical initiation reaction



If we assume that all the incident light is absorbed by the  $\text{Br}_2$  molecules and that the quantum yield for photodissociation is 1.00, then how does the photochemical rate of dissociation of  $\text{Br}_2$  depend on  $I_{\text{abs}}$ , the number of photons per unit time per unit volume? How does  $d[\text{Br}]/dt$ , the rate of formation of Br, depend on  $I_{\text{abs}}$ ? If you assume that the chain reaction is initiated only by the photochemical generation of Br, then how does  $d[\text{HBr}]/dt$  depend on  $I_{\text{abs}}$ ?

- 29-35.** The ability of enzymes to catalyze reactions can be hindered by **inhibitor molecules**. One of the mechanisms by which an inhibitor molecule works is by competing with the substrate molecule for binding to the active site of the enzyme. We can include this inhibition reaction in a modified Michaelis-Menton mechanism for enzyme catalysis.



In Reaction 2, I is the inhibitor molecule and EI is the enzyme-inhibitor complex. We will consider the case where Reaction 2 is always in equilibrium. Determine the rate laws for  $[\text{S}]$ ,  $[\text{ES}]$ ,  $[\text{EI}]$ , and  $[\text{P}]$ . Show that if the steady-state assumption is applied to ES, then

$$[\text{ES}] = \frac{[\text{E}][\text{S}]}{K_m}$$

where  $K_m = (k_{-1} + k_3)/k_1$  is the Michaelis constant. Now show that the material balance for the enzyme gives

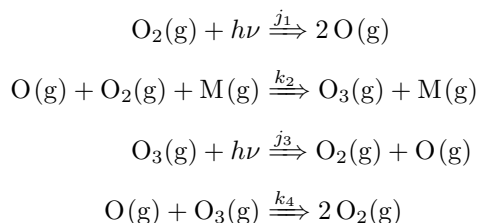
$$[\text{E}]_0 = [\text{E}] + \frac{[\text{E}][\text{S}]}{K_m} + [\text{E}][\text{I}]K_I$$

where  $K_I = [\text{EI}]/[\text{E}][\text{I}]$  is the equilibrium constant for Reaction 2. Use this result to show that the initial reaction rate is given by

$$v = \frac{d[\text{P}]}{dt} = \frac{k_3[\text{E}]_0[\text{S}]}{K_m + [\text{S}] + K_m K_I [\text{I}]} \approx \frac{k_3[\text{E}]_0[\text{S}]_0}{K'_m + [\text{S}]_0} \quad (4)$$

where  $K'_m = K_m(1 + K_I[\text{I}])$ . Note that the second expression in Equation 4 has the same functional form as the Michaelis-Menton equation. Does Equation 4 reduce to the expected result when  $[\text{I}] \rightarrow 0$ ?

**29-47.** A mechanism for ozone creation and destruction in the stratosphere is



where we have used the symbol  $j$  to indicate that the rate constant is for a photochemical reaction. Determine the rate expressions for  $d[\text{O}]/dt$  and  $d[\text{O}_3]/dt$ . Assume that both  $\text{O}(\text{g})$  and  $\text{O}_3(\text{g})$  can be treated by the steady-state approximation and thereby show that

$$[\text{O}] = \frac{2j_1[\text{O}_2] + j_3[\text{O}_3]}{k_2[\text{O}_2][\text{M}] + k_4[\text{O}_3]} \quad (1)$$

and

$$[\text{O}_3] = \frac{k_2[\text{O}][\text{O}_2][\text{M}]}{j_3 + k_4[\text{O}]} \quad (2)$$

Now substitute Equation 1 into Equation 2 and solve the resulting quadratic formula for  $[\text{O}_3]$  to obtain

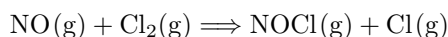
$$[\text{O}_3] = [\text{O}_2] \frac{j_1}{2j_3} \left\{ \left( 1 + \frac{4j_3k_2}{j_1k_4} [\text{M}] \right)^{1/2} - 1 \right\}$$

Typical values for these parameters at an altitude of 30 km are  $j_1 = 2.51 \times 10^{-12} \text{ s}^{-1}$ ,  $j_3 = 3.16 \times 10^{-4} \text{ s}^{-1}$ ,  $k_2 = 1.99 \times 10^{-33} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$ ,  $k_4 = 1.26 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ,  $[\text{O}_2] = 3.16 \times 10^{17} \text{ molecule cm}^{-3}$ , and  $[\text{M}] = 3.98 \times 10^{17} \text{ molecule cm}^{-3}$ . Find  $[\text{O}_3]$  and  $[\text{O}]$  at an altitude of 30 km using Equations 1 and 2. Was the use of the steady-state assumption justified?

## Chapter 30

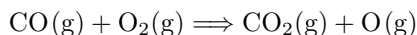
*From McQuarrie and Simon (1997).*

**30-1.** Calculate the hard-sphere collision theory rate constant for the reaction



at 300 K. The collision diameters of NO and  $\text{Cl}_2$  are 370 pm and 540 pm, respectively. The Arrhenius parameters for the reaction are  $A = 3.981 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  and  $E_a = 84.9 \text{ kJ mol}^{-1}$ . Calculate the ratio of the hard-sphere collision theory rate constant to the experimental rate constant at 300 K.

**30-5.** Consider the following bimolecular reaction at 3000 K.



The experimentally determined Arrhenius pre-exponential factor is  $A = 3.5 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ , and the activation energy is  $E_a = 213.4 \text{ kJ mol}^{-1}$ . The hard-sphere collision diameter of  $\text{O}_2$  is 360 pm and that for CO is 370 pm. Calculate the value of the hard sphere line-of-centers model rate constant at 3000 K and compare it with the experimental rate constant. Also compare the calculated and experimental  $A$  values.

## Application

- 1) Name one HW problem you would like to develop into a thought experiment or relate to a literature article.

- 2) Describe how the idea or conclusion from the HW problem applies to the research idea in 1-2 paragraphs (word limit: 300). Once again, this can either be a thought experiment or an experiment found in the literature.
- 3) You do not need to derive any equations in this short discussion. Use your intuition and focus on the big picture.
- 4) Please cite the literature if you link the HW problem to anyone (author names, titles, journal name, volume numbers, and page numbers).