

Chapter 15: Chemical Kinetics
Problems #42, 43, 44, 47, 48, 75, 78

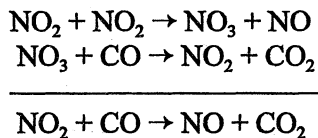
Reaction Mechanisms

42. a. An elementary step (reaction) is one in which the rate law can be written from the molecularity, i.e., from the coefficients in the balanced equation.
- b. The mechanism of a reaction is the series of elementary reactions that occur to give the overall reaction. The sum of all the steps in the mechanism gives the balanced chemical reaction.
- c. The rate determining step is the slowest elementary reaction in any given mechanism.
43. For elementary reactions, the rate law can be written using the coefficients in the balanced equation to determine the orders.
- a. Rate = $k[\text{CH}_3\text{NC}]$ b. Rate = $k[\text{O}_3][\text{NO}]$
- c. Rate = $k[\text{O}_3]$ d. Rate = $k[\text{O}_3][\text{O}]$
- e. Rate = $k[{}^{14}_6\text{C}]$ or Rate = kN where N = the number of ${}^{14}_6\text{C}$ atoms (convention)

44. Since the rate of the slowest elementary step equals the rate of a reaction, then:

$$\text{Rate} = \text{rate of step 1} = k[\text{NO}_2]^2$$

The sum of all steps in a plausible mechanism must give the overall balanced reaction. Summing all steps gives:



47. Let's determine the rate law for each mechanism. If the rate law derived from the mechanism is the same as the experimental rate law, then the mechanism is possible. When deriving rate laws from a mechanism, we must substitute for all intermediate concentrations.
- a. Rate = $k[\text{NO}][\text{O}_2]$ not possible
- b. Rate = $k[\text{NO}_3][\text{NO}]$ and $\frac{[\text{NO}_3]}{[\text{NO}][\text{O}_2]} = K_{\text{eq}} = k_1/k_{-1}$ or $[\text{NO}_3] = K_{\text{eq}}[\text{NO}][\text{O}_2]$
Rate = $kK_{\text{eq}}[\text{NO}]^2[\text{O}_2]$ possible
- c. Rate = $k[\text{NO}]^2$ not possible
- d. Rate = $k[\text{N}_2\text{O}_2]$ and $[\text{N}_2\text{O}_2] = K_{\text{eq}}[\text{NO}]^2$ where $K_{\text{eq}} = k_1/k_{-1}$, Rate = $kK_{\text{eq}}[\text{NO}]^2$ not possible

48. a. This rate law occurs when the first step is rate determining.

$$\text{Rate} = k_1[\text{Br}_2] = k'[\text{Br}_2]$$

- b. This rate law occurs when the second step is rate determining and the first step is a fast equilibrium step.

Rate = $k_2[\text{Br}][\text{H}_2]$; From the fast equilibrium first step (rate forward = rate reverse):

$$k_1[\text{Br}_2] = k_1[\text{Br}]^2, \quad [\text{Br}] = (k_1/k_{-1})^{1/2}[\text{Br}_2]^{1/2}$$

Substituting into the rate equation:

$$\text{Rate} = k_2(k_1/k_{-1})^{1/2}[\text{Br}_2]^{1/2}[\text{H}_2] = k''[\text{H}_2][\text{Br}_2]^{1/2}$$

- c. From a, $k' = k_1$; From b, $k'' = k_2(k_1/k_{-1})^{1/2}$

Additional Exercises

75. Rate = $k[\text{I}^-]^x[\text{OCl}^-]^y[\text{OH}^-]^z$; Comparing the first and second experiments:

$$\frac{18.7 \times 10^{-3}}{9.4 \times 10^{-3}} = \frac{k(0.0026)^x (0.012)^y (0.10)^z}{k(0.0013)^x (0.012)^y (0.10)^z}, \quad 2.0 = 2.0^x, \quad x = 1$$

Comparing the first and third experiments:

$$\frac{9.4 \times 10^{-3}}{4.7 \times 10^{-3}} = \frac{k(0.0013) (0.012)^y (0.10)^z}{k(0.0013) (0.0060)^y (0.10)^z}, \quad 2.0 = 2.0^y, \quad y = 1$$

Comparing the first and sixth experiments:

$$\frac{4.7 \times 10^{-3}}{9.4 \times 10^{-3}} = \frac{k(0.0013) (0.012) (0.20)^z}{k(0.0013) (0.012) (0.10)^z}, \quad 1/2 = 2.0^z, \quad z = -1$$

$$\text{Rate} = \frac{k[\text{I}^-][\text{OCl}^-]}{[\text{OH}^-]}; \quad \text{The presence of OH}^- \text{ decreases the rate of the reaction.}$$

For the first experiment:

$$\frac{9.4 \times 10^{-3} \text{ mol}}{\text{L s}} = k \frac{(0.0013 \text{ mol/L}) (0.012 \text{ mol/L})}{(0.10 \text{ mol/L})}, \quad k = 60.3 \text{ s}^{-1} = 60. \text{ s}^{-1}$$

For all experiments, $k_{\text{mean}} = 60. \text{ s}^{-1}$.

78. The pressure of a gas is directly proportional to concentration. Therefore, we can use the pressure data to solve the problem since $-d[\text{SO}_2\text{Cl}_2]/dt \propto -d P_{\text{SO}_2\text{Cl}_2}/dt$.

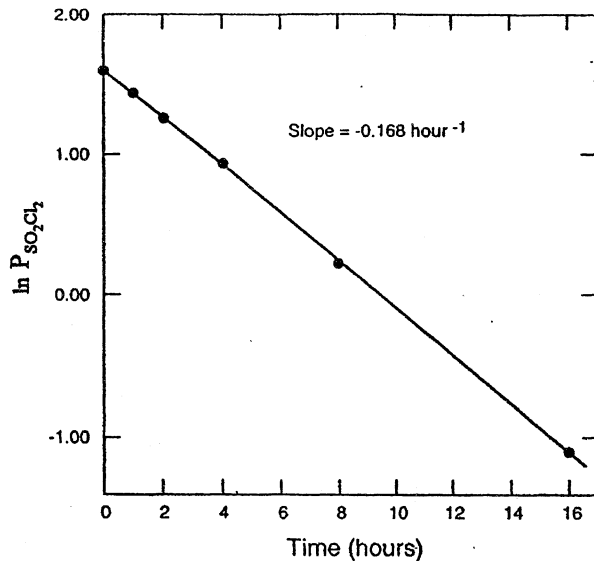
$\text{SO}_2\text{Cl}_2(\text{g}) \rightarrow \text{SO}_2(\text{g}) + \text{Cl}_2(\text{g})$; Let P_0 = initial partial pressure of SO_2Cl_2 .

If $x = P_{\text{SO}_2}$ at some time, then $x = P_{\text{SO}_2} = P_{\text{Cl}_2}$ and $P_{\text{SO}_2\text{Cl}_2} = P_0 - x$.

$P_{\text{tot}} = P_{\text{SO}_2\text{Cl}_2} + P_{\text{SO}_2} + P_{\text{Cl}_2} = P_0 - x + x + x$, $P_{\text{tot}} = P_0 + x$, $P_{\text{tot}} - P_0 = x$

At time = 0 hour, $P_{\text{tot}} = P_0 = 4.93$ atm. The data for other times are:

Time (hour)	0.00	1.00	2.00	4.00	8.00	16.00
P_{tot} (atm)	4.93	5.60	6.34	7.33	8.56	9.52
$P_{\text{SO}_2\text{Cl}_2}$ (atm)	4.93	4.26	3.52	2.53	1.30	0.34
$\ln P_{\text{SO}_2\text{Cl}_2}$	1.595	1.449	1.258	0.928	0.262	-1.08



Since pressure of a gas is proportional to concentration and since the $\ln P_{\text{SO}_2\text{Cl}_2}$ vs. time plot is linear, then the reaction is first order in SO_2Cl_2 .

- a. Slope of $\ln(P)$ vs. t plot is $-0.168 \text{ hour}^{-1} = -k$, $k = 0.168 \text{ hour}^{-1} = 4.67 \times 10^{-5} \text{ s}^{-1}$; Since concentration units don't appear in first order rate constants, then this value of k determined from pressure data will be the same as if concentration data in molarity units were used.
- b. $t_{1/2} = \frac{\ln 2}{k} = \frac{0.6931}{0.168 \text{ h}^{-1}} = 4.13 \text{ hour}$

c. After 0.500 hr: $\ln P_{\text{SO}_2\text{Cl}_2} = -kt + \ln P_0 = -(0.168 \text{ h}^{-1})(0.500 \text{ h}) + \ln 4.93$

$$\ln P_{\text{SO}_2\text{Cl}_2} = -0.0840 + 1.595 = 1.511, P_{\text{SO}_2\text{Cl}_2} = e^{1.511} = 4.53 \text{ atm}$$

$$P_{\text{Cl}_2} = P_{\text{SO}_2} = 4.93 \text{ atm} - 4.53 \text{ atm} = 0.40 \text{ atm}$$

$$P_{\text{tot}} = P_{\text{SO}_2\text{Cl}_2} + P_{\text{Cl}_2} + P_{\text{SO}_2} = 4.53 + 0.40 + 0.40 = 5.33 \text{ atm}$$

After 12.0 hours: $\ln P_{\text{SO}_2\text{Cl}_2} = -(0.168 \text{ h}^{-1})(12.0 \text{ h}) + \ln 4.93 = -0.42$

$$P_{\text{SO}_2\text{Cl}_2} = e^{-0.42} = 0.66 \text{ atm}, P_{\text{SO}_2} = 4.93 - 0.66 = 4.27 \text{ atm}, P_{\text{Cl}_2} = 4.27 \text{ atm}$$

$$P_{\text{tot}} = 0.66 + 4.27 + 4.27 = 9.20 \text{ atm}$$

d. $\ln \left(\frac{P_{\text{SO}_2\text{Cl}_2}}{P_0} \right) = -0.168 \text{ h}^{-1} (20.0 \text{ hr}) = -3.36, \left(\frac{P_{\text{SO}_2\text{Cl}_2}}{P_0} \right) = e^{-3.36} = 3.47 \times 10^{-2}$

$$\text{Fraction left} = 0.0347 = 3.47\%$$