

19. The data in the table are for the reaction of  $\text{NO}_2$  and  $\text{Cl}_2$  to form  $\text{NO}_2\text{Cl}$  and  $\text{NO}_2\text{Cl}_2$ .

a. Determine the order of the reaction for each reactant.

$\text{NO}_2$  is second-order, because doubling its concentration quadruples the rate (page 11, 16, 21).

$\text{Cl}_2$  is first-order, because doubling its concentration doubles the rate (page 11, 16, 21).

b. Write the rate law for the reaction.

$$\text{rate} = k[\text{NO}_2]^2[\text{Cl}_2]$$

c. Calculate the rate constant,  $k$ .

$$\text{rate} = k[\text{NO}_2]^2[\text{Cl}_2]$$

$$2.2 \times 10^{-7} = k(0.002)^2(0.001)$$

$$k = 2.7 \times 10^7 \text{ M}^{-2}\text{s}^{-1}$$

d. Calculate the rate for the reaction when  $[\text{NO}_2] = 0.003 \text{ M}$  and  $[\text{Cl}_2] = 0.0001 \text{ M}$ .

$$\text{rate} = k[\text{NO}_2]^2[\text{Cl}_2] = (2.7 \times 10^7)(0.003)^2(0.0001)$$

$$\text{rate} = 2.1 \times 10^{-7} \text{ M} \cdot \text{s}^{-1} = 2.1 \times 10^{-7} \text{ M/s}$$

e. Calculate the  $k$  when  $[\text{Cl}_2] = 0.0001 \text{ M}$ , holding the second term constant.

$$\text{rate} = k[\text{NO}_2]^2[\text{Cl}_2] = k(0.002)^2(0.0001) = 0.0004$$

From the **MOLE RATIO** in the **CBACHIVE** in  $\text{NO}_2 + \text{Cl}_2 \rightleftharpoons \text{NO}_2\text{Cl} + \text{NO}_2\text{Cl}_2$  and  $\text{Cl}_2 + \text{NO}_2\text{Cl}_2 \rightleftharpoons \text{NO}_2 + 2\text{NO}_2\text{Cl}$ .

From the **STOIC. COEFFICIENTES**,  $1/0.0001 = 1/0.002 = 0.0004$ .

f. Calculate the rate under the conditions given in "e."

$$\text{rate} = k[\text{NO}_2]^2[\text{Cl}_2] = 0.0004 \text{ M} \cdot \text{s}^{-1}$$

g. When first-order in nitrogen, as  $\text{NO}_2$  with the steady-state concentrations, would the initial rate still be  $2.1 \times 10^{-7} \text{ M/s}$ ? Explain your answer.

Ans:  $\text{NO}_2$  is present in stoichiometric amounts, so the initial reaction rate is independent of the initial  $\text{NO}_2$  concentration.  $\text{Cl}_2$  is limiting because when the  $\text{NO}_2$  concentration would be larger, there would be more  $\text{NO}_2\text{Cl}_2$ .

20. Calculate equilibrium constant values for the following reactions:

$\text{NO}_2\text{Cl}_2 \rightleftharpoons \text{NO}_2 + \text{NO}_2\text{Cl}$

Initial concentration, M	Final concentration, M	Change in concentration, M
0.002	0.001	0.001 $\times 10^{-3}$
0.002	0.001	0.001 $\times 10^{-3}$
0.002	0.001	0.001 $\times 10^{-3}$

a. Without using steady-state concentrations?

$$\text{rate} = k[\text{NO}_2]^2[\text{Cl}_2]$$

b. Without using the order of the reaction with respect to  $\text{NO}_2$ ?

Initial values

c. Without using the order with respect to  $\text{Cl}_2$ ?

Initial values

d. Without using the overall order of the reaction?

Initial values

e. Without using the values of the rate constants,  $k$ , with units?

$$\text{rate} = k[\text{NO}_2]^2[\text{Cl}_2]$$

$$2.2 \times 10^{-7} \text{ M} \cdot \text{s}^{-1} = k(0.002)^2(0.001)$$

$$k = 4.5 \times 10^7 \text{ M}^{-2}\text{s}^{-1}$$

f. Assuming that  $k$  for the  $\text{NO}_2$  term is  $0.0004 \text{ M}^{-1}\text{s}^{-1}$ , rather than  $2.2 \times 10^{-7}$ ?

$$\text{rate} = k[\text{NO}_2]^2[\text{Cl}_2] = 0.0004 \times (0.002)^2(0.001) = 0.0004$$

From the **MOLE RATIO** in  $\text{NO}_2 + \text{NO}_2\text{Cl}_2 \rightleftharpoons \text{NO}_2 + \text{NO}_2\text{Cl}$  and  $\text{Cl}_2 + \text{NO}_2\text{Cl}_2 \rightleftharpoons \text{NO}_2 + 2\text{NO}_2\text{Cl}$ .

g. Calculate the rate for the overall reaction dependent on "f."  $\text{rate} = k[\text{NO}_2]^2[\text{Cl}_2] = 0.0004 \times (0.002)^2(0.001) = 0.0004$

$$\text{rate} = k[\text{NO}_2]^2[\text{Cl}_2]$$

$$\text{rate} = k[\text{NO}_2]^2[\text{Cl}_2] = 0.0004 \times (0.002)^2(0.001)$$

Reaction Conditions		Rate of Reaction and Rate Constants
Initial	Final	
0.002	0.001	
0.002	0.001	$2.2 \times 10^{-7}$
0.002	0.001	$0.0004 \times 10^{-3}$
0.002	0.001	$4.5 \times 10^7 \text{ M}^{-2}\text{s}^{-1}$

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