ChemActivity **57**

Rates of Chemical Reactions (II)

(How Does the Concentration of Reactants Affect the Rate?)

Model 1: The Rate of a Reaction Varies with Time.

We have previously defined the rate of reaction as

$$\text{rate} = -\frac{\Delta(\text{reactant})}{\Delta\text{time}}$$

for any chemical reactant with a stoichiometric coefficient of 1 in the balanced chemical equation.

A better measure of the rate of a reaction is the *instantaneous rate of reaction,* generally written as

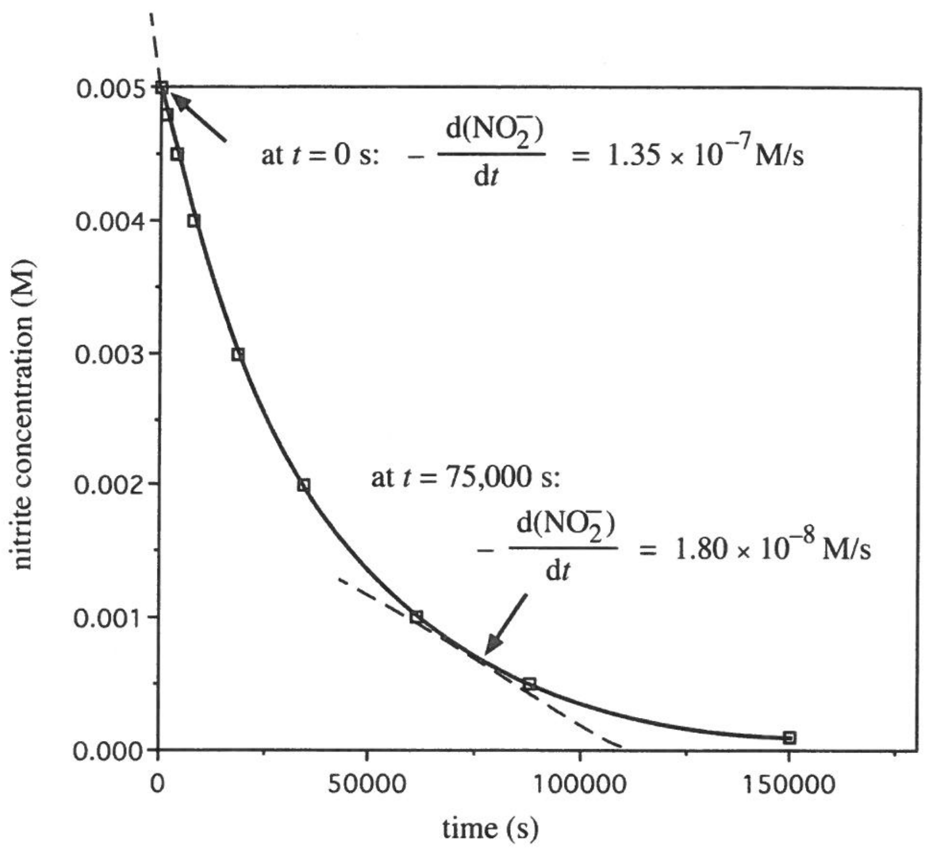
$$\text{rate} = -\frac{\mathrm{d}(\text{reactant})}{\mathrm{d}t}$$

The value of the instantaneous rate of reaction (for reactants with a stoichiometric coefficient of one in the balanced chemical equation) can be obtained by plotting the concentration of the reactant versus time, drawing a tangent to the curve, and determining the slope of the line.

Figure 1. **Nitrite concentration versus time for the reaction of ammonium ion with nitrite ion.**

$$NH_4^+(aq) + NO_2^-(aq) \rightleftharpoons N_2(g) + 2\,H_2O(\ell)$$

$$(NO_2^-)_o = 0.00500\ \text{M} \qquad (NH_4^+)_o = 0.100\ \text{M}$$



Critical Thinking Questions

1. What is the rate of reaction at $t = 0$ s?

2. What is the rate of reaction at $t = 75{,}000$ s?

3. How does the rate of reaction change as (NO_2^-) decreases?

4. Estimate the value of the rate of reaction at $t = 175{,}000$ s. Explain your reasoning.

Model 2: The Effect of Concentration on Reaction Rate.

$$NH_4^+(aq) + NO_2^-(aq) \rightleftharpoons N_2(g) + 2\,H_2O(\ell)$$

Table 1. Initial reaction rates for several experiments at 25 °C.

Experiment	Initial Concentration of NH_4^+ (M)	Initial Concentration of NO_2^- (M)	Initial Rate of Reaction (M /sec)
1	0.100	0.0050	1.35×10^{-7}
2	0.100	0.010	2.70×10^{-7}
3	0.200	0.010	5.40×10^{-7}

Critical Thinking Questions

5. For the three experiments in Table 1:

   a) Which experiment has the fastest initial rate of reaction?

   b) Which experiment has the slowest initial rate of reaction?

   c) Why do you think the initial rates of reaction are different in the three experiments?

6. Comparing experiments **1** and **2** only:

   a) Are the initial concentrations of NH_4^+ the same? If not, what is the ratio of the concentrations expressed as a fraction, $(NH_4^+)_2/(NH_4^+)_1$?

   b) Are the initial concentrations of NO_2^- the same? If not, what is the ratio of the concentrations expressed as a fraction, $(NO_2^-)_2/(NO_2^-)_1$?

   c) Are the initial rates of reaction the same? If not, what is the ratio of the rates of reaction expressed as a fraction, initial rate_2/initial rate_1?

   d) Based on the answers to parts a) – c) above, can you determine whether or not the initial rate of reaction depends on the initial (NH_4^+)? Why or why not?

e) Based on the answers to parts a) – c) above, can you determine whether or not the initial rate of reaction depends on the initial (NO_2^-)? Why or why not?

f) Based on your answers to a) – c), does the rate of reaction appear to be proportional to (NO_2^-) raised to some power? If so, what is the power?

7. Comparing experiments **2** and **3** only:

a) Are the initial concentrations of NH_4^+ the same? If not, what is the ratio of the concentrations expressed as a fraction, $(NH_4^+)_3/(NH_4^+)_2$?

b) Are the initial concentrations of NO_2^- the same? If not, what is the ratio of the concentrations expressed as a fraction, $(NO_2^-)_3/(NO_2^-)_2$?

c) Are the initial rates of reaction the same? If not, what is the ratio of the rates of reaction expressed as a fraction, initial $rate_3$/initial $rate_2$?

d) Based on the answers to parts a) – c) above, can you determine whether or not the initial rate of reaction depends on the initial (NH_4^+)? Why or why not?

e) Based on the answers to parts a) – c) above, can you determine whether or not the initial rate of reaction depends on the initial (NO_2^-)? Why or why not?

f) Based on your answers to a) – c), does the rate of reaction appear to be proportional to (NH_4^+) raised to some power? If so, what is the power?

Model 3: The Rate Law.

Often the rate of reaction is found to be proportional to the concentration of a reactant raised to some power (usually an integer such as 0, 1, 2, ...). For example, if

$$\text{rate} = k\,(\text{R})^x \qquad \text{then,}$$

$$\frac{\text{initial rate}_2}{\text{initial rate}_1} = \frac{k(\text{R})_2^x}{k(\text{R})_1^x} = \left(\frac{(\text{R})_2}{(\text{R})_1}\right)^x$$

where initial rate$_i$ = the initial rate of experiment i
(R)$_i$ = the initial concentration of the reactant R for experiment i

The relationship between the rate of a reaction and the concentrations of reactants is known as the **rate law.** An example of a typical rate law is

$$\text{rate} = k\,(NH_4^+)^x\,(NO_2^-)^y \tag{1}$$

where k is the proportionality constant, known as the **rate constant**, and x and y are the exponents described previously. The rate constant is characteristic of a particular reaction at a given temperature. The exponents are often referred to as the order of the reaction with respect to the respective reactants. For example, if $x = 3$, we say that the reaction is third order with respect to NH_4^+. The rate constant and the exponents (or orders) can be determined by experiment only.

Critical Thinking Questions

8. Based on your answers to CTQ 7, determine the order of the reaction in the Model 2 with respect to NH_4^+.

9. Based on your answers to CTQ 6 determine the order of the reaction in the Model 2 with respect to NO_2^-.

10. a) Based on your answers to CTQs 8 and 9, calculate the value of the rate constant k in the rate law for the reaction using

    i) data from Experiment 1

    ii) data from Experiment 2

    iii) data from Experiment 3

b) Compare the three answers from part a). Explain why the relative values are reasonable.

Table 2. Experimental rate laws for several chemical reactions.

Reaction	Experimental Rate Law
$CH_3Br(aq) + OH^-(aq) \rightleftharpoons CH_3OH(aq) + Br^-(aq)$	rate = $k\,(CH_3Br)$
$2NO(g) + O_2(g) \rightleftharpoons 2\,NO_2(g)$	rate = $k\,(NO)^2\,(O_2)$
$2\,HI(g) \rightleftharpoons H_2(g) + I_2(g)$	rate = $k\,(HI)^2$
$NH_4^+(aq) + NO_2^-(aq) \rightleftharpoons N_2(g) + 2\,H_2O(\ell)$	rate = $k\,(NH_4^+)\,(NO_2^-)$
$BrO_3^-(aq) + 5Br^-(aq) + 6H^+(aq) \rightleftharpoons 3Br_2(aq) + H_2O$	rate = $k\,(BrO_3^-)(Br^-)\,(H^+)^2$
$CH_3CHO(g) \rightleftharpoons CH_4(g) + CO(g)$	rate = $k\,(CH_3CHO)^{3/2}$

Critical Thinking Questions

11. Based on the data in Table 2, is the order of a reaction with respect to a particular species always equal to its stoichiometric coefficient in the chemical equation?

12. Comment on the appropriateness of the following methods to determine the order of a reaction.

a) Examine the stoichiometric coefficients in the chemical equation. In this method, the order of a reaction with respect to a component is equal to the stoichiometric coefficient of that component in the chemical equation.

b) Perform experiments. In this method, the order of a reaction with respect to a component is determined by how the reaction rate changes when the concentration(s) is changed.

Exercises

1. What is the initial rate of production of N_2 in experiment 3 of Table 1?

2. The following initial reaction rates were observed for the oxidation of Fe^{2+} by Ce^{4+}:

Experiment	Initial Concentration of Ce^{4+} (M)	Initial Concentration of Fe^{2+} (M)	Initial Rate of Reaction (M /sec)
1	1.5×10^{-5}	2.5×10^{-5}	3.79×10^{-7}
2	1.5×10^{-5}	5.0×10^{-5}	7.58×10^{-7}
3	3.0×10^{-5}	5.0×10^{-5}	1.52×10^{-6}

a) Determine the order of the reaction with respect to Ce^{4+} and with respect to Fe^{2+}.
b) Write the rate law for this reaction.
c) Calculate the rate constant, *k*, and give its units.
d) Predict the initial reaction rate for a solution in which (Ce^{4+}) is 1.0×10^{-5} M and (Fe^{2+}) is 1.8×10^{-5} M.

3. Determine the rate law and evaluate the rate constant for the following reaction:

$$2\,NO(g) + Br_2(g) \rightleftharpoons 2\,NOBr(g)$$

Experiment	$(NO)_o$ (M)	$(Br_2)_o$ (M)	Initial Rate of Reaction (M/min)
1	0.10	0.10	1.30×10^{-3}
2	0.20	0.10	5.20×10^{-3}
3	0.20	0.30	1.56×10^{-2}

4. The following reaction was studied experimentally at 25 °C.

$$S_2O_8^{2-}(aq) + 2\,I^-(aq) \rightleftharpoons I_2(aq) + 2\,SO_4^{2-}(aq)$$

The reaction was found to be first order in I^- and first order in $S_2O_8^{2-}$. A reaction was run with $(I^-)_o = 0.080$ M and $(S_2O_8^{2-})_o = 0.040$ M. The initial rate of formation of I_2 was found to be $1.25 \times 10^{-6}\ \frac{\text{mole}}{\text{liter s}}$. Provide an expression for the rate law for this reaction, and determine the initial rate of formation of I_2 when $(I^-)_o = 0.080$ M and $(S_2O_8^{2-})_o = 0.060$ M.

5. Indicate whether the following statement is true or false and explain your reasoning.

   The rate law for a reaction can be obtained by examining the chemical equation for the reaction.

Problems

1. One of the major irritants found in smog is formaldehyde, $CH_2O(g)$, formed by the reaction of ethene and ozone in the atmosphere:

   $$C_2H_4(g) + 2\ O_3(g) \rightleftarrows 4\ CH_2O(g) + O_2(g)$$

   From the following initial rate data, deduce the rate law for this reaction. Clearly indicate how you arrived at your answer.

Experiment	Initial Concentration of O_3 (M)	Initial Concentration of C_2H_4 (M)	Initial Rate of Reaction (M /sec)
1	0.5×10^{-7}	1.0×10^{-8}	1.0×10^{-12}
2	1.5×10^{-7}	1.0×10^{-8}	3.0×10^{-12}
3	1.0×10^{-7}	2.0×10^{-8}	4.0×10^{-12}

2. For the following reaction:

   $$2\ HgCl_2(aq) + C_2O_4^{2-}(aq) \rightleftarrows Hg_2Cl_2(s) + 2\ Cl^-(aq) + 2\ CO_2(g)$$

Experiment	Initial Concentration of $HgCl_2$ (M)	Initial Concentration of $C_2O_4^{2-}$ (M)	Initial Rate of Reaction (M /sec)
1	0.096	0.13	2.1×10^{-7}
2	0.096	0.21	5.5×10^{-7}
3	0.171	0.21	9.8×10^{-7}

   a) Determine the order of the reaction with respect to $HgCl_2$ and with respect to $C_2O_4^{2-}$.
   b) Write the rate law for this reaction.
   c) Calculate the rate constant and give its units.

3. Consider the reaction

$$2\ UO_2^+(aq) + 4\ H^+(aq) \rightleftharpoons U^{4+}(aq) + UO_2^{2+}(aq) + 2\ H_2O(\ell)$$

a) From the following initial rate data, deduce the rate law for this reaction. Clearly indicate how you arrived at your answer. b) Find the rate constant k, including units, for the reaction above.

Experiment	Initial Concentration of UO_2^+ (M)	Initial Concentration of H^+ (M)	Initial Rate of Reaction (M /sec)
1	0.0012	0.22	4.12×10^{-5}
2	0.0012	0.35	6.55×10^{-5}
3	0.0030	0.35	4.10×10^{-4}

4. The following data were collected for the reaction:

$$2\ NO(g) + O_2(g) \rightleftharpoons 2\ NO_2(g)$$

Initial NO Concentration (mol/L)	Initial O_2 Concentration (mol/L)	Initial Rate of reaction (mol/Ls)
5.38×10^{-3}	5.38×10^{-3}	1.91×10^{-5}
8.07×10^{-3}	5.38×10^{-3}	4.30×10^{-5}
13.45×10^{-3}	5.38×10^{-3}	11.94×10^{-5}
8.07×10^{-3}	6.99×10^{-3}	5.59×10^{-5}
8.07×10^{-3}	9.69×10^{-3}	7.75×10^{-5}

What is the rate law for the reaction?