

# 15 • Chemical Kinetics

## RATE LAWS

**Big Ideas** (This is Section 15.3 in the textbook, pages 694 – 700):

- One factor that speeds up a reaction is **CONCENTRATION**.
- Higher concentrations of reactants means there will be **more collisions** between the particles that need to collide to cause a reaction.
- **How much** the rate of a reaction increases gives clues to the step-by-step **mechanism** of a reaction.
- A Rate Law has a **standard format**. For a reaction such as  $A + B \rightarrow C + D$ , the rate law is:

$$\text{Rate} = k[A]^x[B]^y$$

( $x$  = the order of the reaction with respect to A,  $y$  = the order with respect to B and  $k$  = the rate constant)

1. Consider the initial rate data for the reaction,  $A + B \rightarrow C$ :

	[A]	[B]	Rate ( $\text{mol}\cdot\text{L}^{-1}\cdot\text{s}^{-1}$ )
Expt 1	0.10	0.10	2.0
Expt 2	0.10	0.20	4.0
Expt 3	0.20	0.20	32.0

- What is the order of reactant A?
- What is the order of reactant B?
- Write the rate equation for the reaction.
- Calculate the value of the specific rate constant,  $k$ .

2. Consider the initial rate data for the reaction,  $3X + 2Y \rightarrow Z$ :

	[X]	[Y]	Rate ( $\text{mol}\cdot\text{L}^{-1}\cdot\text{s}^{-1}$ )
Expt 1	0.10	0.20	4.0
Expt 2	0.10	0.10	1.0
Expt 3	0.20	0.20	4.0
Expt 4	0.25	0.25	

- What is the order of reactant X?
- What is the order of reactant Y?
- What is the overall order of the reaction?
- Write the rate equation for the reaction.
- Calculate the value of the specific rate constant,  $k$ .

- f. Calculate the rate when the  $[X]$  and  $[Y] = 0.25 \text{ mol}\cdot\text{L}^{-1}$ .

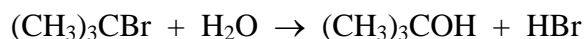
3. Consider the reaction:  $2 \text{NO(g)} + \text{O}_2\text{(g)} \rightarrow 2 \text{NO}_2\text{(g)}$

The following data were obtained from three experiments using the method of initial rates:

	Initial [NO] mol L <sup>-1</sup>	Initial [O <sub>2</sub> ] mol L <sup>-1</sup>	Initial rate NO mol L <sup>-1</sup> s <sup>-1</sup>
Experiment 1	0.010	0.010	$2.5 \times 10^{-5}$
Experiment 2	0.020	0.010	$1.0 \times 10^{-4}$
Experiment 3	0.010	0.020	$5.0 \times 10^{-5}$

- Determine the order of the reaction for each reactant.
- Write the rate equation for the reaction.
- Calculate the rate constant.
- Calculate the rate (in mol L<sup>-1</sup>s<sup>-1</sup>) at the instant when [NO] = 0.015 mol L<sup>-1</sup> and [O<sub>2</sub>] = 0.0050 mol L<sup>-1</sup>
- At the instant when NO is reacting at the rate  $1.0 \times 10^{-4}$  mol L<sup>-1</sup>s<sup>-1</sup>, what is the rate at which O<sub>2</sub> is reacting and NO<sub>2</sub> is forming?

4. The reaction of <sup>t</sup>butyl-bromide (CH<sub>3</sub>)<sub>3</sub>CBr with water is represented by the equation:



The following data were obtained from three experiments using the method of initial rates:

	Initial [(CH <sub>3</sub> ) <sub>3</sub> CBr] mol L <sup>-1</sup>	Initial [H <sub>2</sub> O] mol L <sup>-1</sup>	Initial rate mol L <sup>-1</sup> min <sup>-1</sup>
Experiment 1	$5.0 \times 10^{-2}$	$2.0 \times 10^{-2}$	$2.0 \times 10^{-6}$
Experiment 2	$5.0 \times 10^{-2}$	$4.0 \times 10^{-2}$	$2.0 \times 10^{-6}$
Experiment 3	$1.0 \times 10^{-1}$	$4.0 \times 10^{-2}$	$4.0 \times 10^{-6}$

- What is the order with respect to (CH<sub>3</sub>)<sub>3</sub>CBr?
- What is the order with respect to H<sub>2</sub>O?
- What is the overall order of the reaction?
- Write the rate equation.
- Calculate the rate constant, k, for the reaction.

5. Some problems can be solved “by inspection”, but you can also treat them **mathematically**.

Consider the initial rate data for the reaction,  $A + B \rightarrow C$ :

	[A]	[B]	Rate ( $\text{mol}\cdot\text{L}^{-1}\cdot\text{s}^{-1}$ )
Expt 1	0.10	0.10	$3.0 \times 10^{-5}$
Expt 2	0.10	0.20	$6.0 \times 10^{-5}$
Expt 3	0.20	0.30	$3.6 \times 10^{-4}$

Use the rate law to write a reaction for Experiment 2 / Experiment 1

$$\text{Rate} = k [A]^x [B]^y$$

Experiment 2:

Experiment 1:

Repeat the procedure with Experiment 3 / Experiment 1

$$\text{Rate} = k [A]^x [B]^y$$

Experiment 3:

Experiment 1:

- What is the order of reactant A?
- What is the order of reactant B?
- Write the rate equation for the reaction.
- Calculate the value of the specific rate constant,  $k$ .

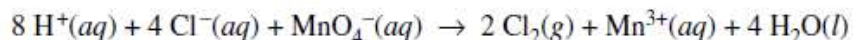
6. The reaction  $2 \text{NO}(\text{g}) + 2 \text{H}_2(\text{g}) \rightarrow \text{N}_2(\text{g}) + 2 \text{H}_2\text{O}(\text{g})$  was studied at  $904^\circ\text{C}$ , and the data in the table were collected.

	Initial [NO] $\text{mol L}^{-1}$	Initial [H <sub>2</sub> ] $\text{mol L}^{-1}$	Initial rate N <sub>2</sub> $\text{mol L}^{-1}\text{s}^{-1}$
Experiment 1	0.420	0.122	0.136
Experiment 2	0.210	0.122	0.0339
Experiment 3	0.105	0.488	0.0339

- Determine the order of the reaction for each reactant.
- Write the rate equation for the reaction.
- Calculate the rate constant at  $904^\circ\text{C}$ .
- Find the rate of appearance of  $\text{N}_2$  at the instant when  $[\text{NO}] = 0.350 \text{ M}$  and  $[\text{H}_2] = 0.205 \text{ M}$ .

**FRQ from the 2010 AP Exam**

You should be able to do the entire question, but for this worksheet, simply do parts (b) and (c).



3.  $\text{Cl}_2(g)$  can be generated in the laboratory by reacting potassium permanganate with an acidified solution of sodium chloride. The net-ionic equation for the reaction is given above.
- (a) A 25.00 mL sample of 0.250 M NaCl reacts completely with excess  $\text{KMnO}_4(aq)$ . The  $\text{Cl}_2(g)$  produced is dried and stored in a sealed container. At 22°C the pressure of the  $\text{Cl}_2(g)$  in the container is 0.950 atm.
- Calculate the number of moles of  $\text{Cl}^-(aq)$  present before any reaction occurs.
  - Calculate the volume, in L, of the  $\text{Cl}_2(g)$  in the sealed container.

An initial-rate study was performed on the reaction system. Data for the experiment are given in the table below.

Trial	$[\text{Cl}^-]$	$[\text{MnO}_4^-]$	$[\text{H}^+]$	Rate of Disappearance of $\text{MnO}_4^-$ in $M \text{ s}^{-1}$
1	0.0104	0.00400	3.00	$2.25 \times 10^{-8}$
2	0.0312	0.00400	3.00	$2.03 \times 10^{-7}$
3	0.0312	0.00200	3.00	$1.02 \times 10^{-7}$

- (b) Using the information in the table, determine the order of the reaction with respect to each of the following. Justify your answers.
- $\text{Cl}^-$
  - $\text{MnO}_4^-$
- (c) The reaction is known to be third order with respect to  $\text{H}^+$ . Using this information and your answers to part (b) above, complete both of the following:
- Write the rate law for the reaction.
  - Calculate the value of the rate constant,  $k$ , for the reaction, including appropriate units.
- (d) Is it likely that the reaction occurs in a single elementary step? Justify your answer.