

Chapter 12

Chemical Kinetics: The Study of Rates of Reaction

Reaction Rates

Chemical Kinetics: study of how fast/slow (rate) a reaction occurs, and the mechanism by which it occurs.

Some reactions happen **VERY** quickly, while others happen **VERY** slowly. We observe how fast the reaction occurs. Balanced equation provides no information on rate of reaction.

Examples:

Rate of reaction=

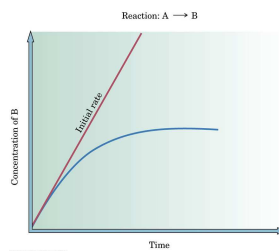
Consider the theoretical reaction: $aA \rightarrow bB$

Write the expressions for.....

Rate of appearance of product =

Rate of disappearance of reactant =

NOTE: Pure product may never be obtained!!

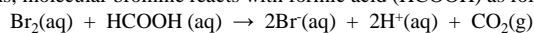


Sample Questions

1. Consider the following equation: $2\text{N}_2\text{O}_5(\text{g}) \rightarrow 4\text{NO}_2(\text{g}) + \text{O}_2(\text{g})$
 From the following experimental data calculate the rate of disappearance of N_2O_5 , and the rates of appearances of NO_2 and O_2 , over the time intervals: 0-500 s, 500-1000s, 1000-1500 s.

<u>Time (s)</u>	<u>[N₂O₅]</u>	
0	5.00	Is the reaction rate constant?
500	3.52	If not, what does it depend on?
1000	2.48	What is the difference between $-\Delta[\text{N}_2\text{O}_5]/\Delta t$ and $-d[\text{N}_2\text{O}_5]/dt$?
1500	1.75	

2. In aqueous solutions, molecular bromine reacts with formic acid (HCOOH) as follows:



From the following experimental data calculate the rate of disappearance of Br_2 , and the rate of appearances of Br^- and CO_2 , over the time intervals: 0-50 s, 50-100 s, and 100-150 s.

(0-50 s = 3.8×10^{-5} M/s; 3.8×10^{-5} M/s; 7.6×10^{-5} M/s; 50-100 s = 3.3×10^{-5} M/s; 3.3×10^{-5} M/s; 6.6×10^{-5} M/s; and 100-150 s = 2.72×10^{-5} M/s; 2.72×10^{-5} M/s; 5.44×10^{-5} M/s)

<u>Time(s)</u>	<u>[Br₂]</u>	<u>Time(s)</u>	<u>[Br₂]</u>	<u>Time(s)</u>	<u>[Br₂]</u>
0.0	0.0120	150.0	0.00710	300.0	0.00420
50.0	0.0101	200.0	0.00596	350.0	0.00353
100.0	0.00846	250.0	0.00500	400.0	0.00296

Rate of Reaction and the Slope

Instantaneous reaction rate: rate at each individual point on the curve

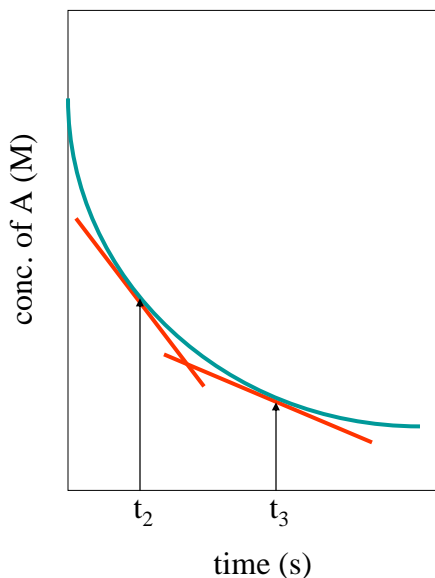
Graphically:

- 1.
- 2.

Mathematically:

- 1.
- 2.

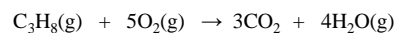
$$\frac{-d[A]}{dt} = \frac{-df(t)}{dt}$$



Relating Rates of Appearance and Disappearance

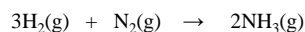
How related?

1. Consider the following reaction:



If at a given moment C_3H_8 is reacting at rate of $0.400 \text{ mol L}^{-1} \text{ s}^{-1}$, what are the rates of formation of CO_2 and H_2O ? What is the rate of disappearance of O_2 ?

2. Hydrogen and nitrogen react to form ammonia according to the equation



If hydrogen is consumed at a rate of 0.50 M s^{-1} , what is the rate at which nitrogen is consumed, and what is the rate at which ammonia is produced?

Rate Laws

It turns out that the rate of a reaction is **proportional** to the concentrations of the different **reactants** raised to *experimentally determined* exponents.

A General **Rate Law** can be written for any reaction:



Rate =

Where:

k = specific rate constant

- 1.
- 2.
- 3.

m and **n** are **order of reaction** with respect to each reactant

- 1.

Rate Law Examples

- The reaction: $\text{NO}_2(\text{g}) + \text{CO}(\text{g}) \rightarrow \text{CO}_2(\text{g}) + \text{NO}(\text{g})$ at 200°C is known to be second order in NO_2 and zeroth order in CO .
 - Write the rate law for this reaction.
 - What is the overall reaction order for this reaction?
 - What will happen to the reaction rate if the $[\text{NO}_2]$ is doubled?
 - What will happen to the reaction rate if the $[\text{CO}]$ is halved?
 - What are the units on k ?

- The gas-phase reaction of nitric oxide and bromine yields nitrosyl bromide:
$$2\text{NO}(\text{g}) + \text{Br}_2(\text{g}) \rightarrow 2\text{NOBr}(\text{g})$$
The rate law is $\text{rate} = k[\text{NO}]^2[\text{Br}_2]$. What is the order of reaction with respect to each of the reactants, and what is the overall reaction order? What will happen to the reaction rate if $[\text{NO}]$ is tripled? if $[\text{Br}_2]$ is doubled? if $[\text{Br}_2]$ halved? What are the units of k ?

- Bromomethane is converted to methanol in an alkaline solution. The reaction is first order in each reactant.
$$\text{CH}_3\text{Br}(\text{aq}) + \text{OH}^-(\text{aq}) \rightarrow \text{CH}_3\text{OH}(\text{aq}) + \text{Br}^-(\text{aq})$$
 - Write the rate law. (rate= $k[\text{CH}_3\text{Br}][\text{OH}^-]$)
 - How does the reaction rate change in the OH^- concentration is decreased by a factor of 5? (rate will decrease by a factor of 5)
 - What is the change in rate if the concentration of both reactants are doubled? (rate will increase by a factor of 4)

Factors That Affect the Reaction Rate

-
-
-
-

Example: Consider the heterogeneous reaction studied during
Exp #2: Chemical Reaction Rates.



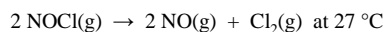
Reaction Rate =

Method of Initial Rates

Experimental method used to determine orders of reaction (m,n) and k.

Best way to learn this method is by example....

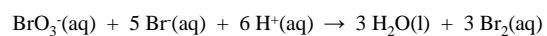
1. Use the method of initial rates to find the **rate law** for the following reaction:



<u>[NOCl]</u>	<u>Initial Rate of Formation of NO</u>
0.30 M	3.60×10^{-9} M/s
0.60 M	1.44×10^{-8} M/s
0.90 M	3.24×10^{-8} M/s

What is the value of the specific rate constant? How much will the rate of this reaction change if the initial concentration of NOCl is increased from 0.30 M to 1.2 M?

2. Find the **rate law** for the following reaction given the data shown below.



<u>[BrO₃⁻]</u>	<u>[Br⁻]</u>	<u>[H⁺]</u>	<u>-d[BrO₃⁻]/dt</u>
0.10 M	0.10 M	0.10 M	0.0012 M/s
0.20 M	0.10 M	0.10 M	0.0024 M/s
0.10 M	0.30 M	0.10 M	0.0035 M/s
0.20 M	0.10 M	0.15 M	0.0054 M/s
0.30 M	0.30 M	0.30 M	??

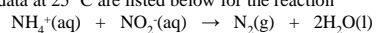
What is the value of the specific rate constant and what are its units? Calculate the rate of disappearance of BrO₃⁻ for the last trial.

3. At 600 °C, acetone (CH_3COCH_3) decomposes to ketone ($\text{CH}_2=\text{C}=\text{O}$) and various hydrocarbons. Initial rate data are given below:

$[\text{CH}_3\text{COCH}_3]_0$	Initial rate of decomposition of CH_3COCH_3 (M/s)
$6.0 \times 10^{-3} \text{ M}$	5.2×10^{-5}
$9.0 \times 10^{-3} \text{ M}$	7.8×10^{-5}

- Determine the rate law.
- Calculate the value of the specific rate constant.
- Calculate the initial rate decomposition when the initial acetone concentration is $1.8 \times 10^{-3} \text{ M}$.
- How much will the reaction rate increase if the initial concentration of CH_3COCH_3 is increased from $6.0 \times 10^{-3} \text{ M}$ to $2.4 \times 10^{-2} \text{ M}$.

4. Initial rate data at 25 °C are listed below for the reaction



$[\text{NH}_4^+]_0$	$[\text{NO}_2^-]_0$	Initial rate of consumption of nitrite (M/s)
0.24 M	0.10 M	7.2×10^{-6}
0.12 M	0.10 M	3.6×10^{-6}
0.12 M	0.15 M	5.4×10^{-6}

- What is the rate law? (rate = $k[\text{NH}_4^+][\text{NO}_2^-]$)
- What is the value of the rate constant? ($3.0 \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$)
- What is the initial rate when the initial concentrations are $[\text{NH}_4^+] = 0.39 \text{ M}$ and $[\text{NO}_2^-] = 0.052 \text{ M}$? ($6.1 \times 10^{-6} \text{ M s}^{-1}$)