

Chemical Kinetics and the Nucleus, a Chemist's View

Chapter 12 and 19

Homework

- Due with test
- AP Practice Test at the end of chapter 12 between 509-510

Kinetics

- **Chemical kinetics** is the study of the changes in concentrations of reactants or products as a function of time.
- It is the study of **reaction rates**.
- Each reaction has its own characteristic rate.
 - The reactions may be slow, fast, or reversible.

What affects reactions rates

- **Concentration:** molecules must collide in order to react.
- **Physical state:** molecules must mix in order to collide.
- **Temperature:** molecules must collide with enough energy to react.
- The use of a **catalyst/inhibitor**

Reaction Rate

- Change in concentration of a reactant or product per unit time.

$$\text{Rate} = \frac{\text{concentration of A at time } t_2 - \text{concentration of A at time } t_1}{t_2 - t_1}$$

$$= \frac{\Delta[A]}{\Delta t}$$

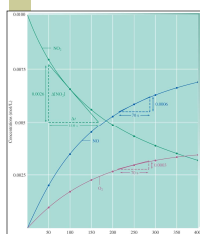
[A] means concentration of A in mol/L; A is the reactant or product being considered.

The Decomposition of Nitrogen Dioxide

Table 13.1 Concentrations of Reactant and Products as a Function of Time for the Reaction $2\text{NO}_2(\text{g}) \rightarrow 2\text{NO}(\text{g}) + \text{O}_2(\text{g})$ (at 300°C)

Time (± 1 s)	Concentration (mol/L)		
	NO_2	NO	O_2
0	0.0100	0	0
50	0.0079	0.0021	0.0011
100	0.0065	0.0035	0.0018
150	0.0055	0.0045	0.0023
200	0.0048	0.0052	0.0028
250	0.0043	0.0057	0.0029
300	0.0038	0.0062	0.0031
350	0.0034	0.0066	0.0033
400	0.0031	0.0069	0.0035

Decomposition of Nitrogen Dioxide



Rate terms

- A **reaction rate** is the change in concentration of a reactant or a product per unit of time.
- An **average rate** is the change in concentration of reactants (or products) over a finite time period.
- An **instantaneous rate** is the reaction rate at a particular time, given by the slope of a tangent to a plot of reactant concentration vs. time.

Rate terms

- An **initial rate** is the instantaneous rate at the point at which the reactants are mixed, that is, at $t = 0$.

Rate Law

- ♦ **Rate law**- An expression showing how the rate depends on the concentrations of reactants.
- ♦ For the decomposition of nitrogen dioxide:
 $2\text{NO}_2(\text{g}) \rightarrow 2\text{NO}(\text{g}) + \text{O}_2(\text{g})$
 Rate = $k[\text{NO}_2]^n$:
 - k = rate constant
 - n = order of the reactant

Rate Law

- Rate = $k[\text{NO}_2]^n$
- ♦ The concentrations of the products do not appear in the rate law because this particular reaction rate is being studied under conditions where the reverse reaction does not contribute to the overall rate.

Rate Law

- Rate = $k[\text{NO}_2]^n$
- ♦ **The value of the exponent n must be determined by experiment; it cannot be written from the balanced equation.**

Units of k

- ♦ For whatever reason, the AP test loves to ask for the correct units of k .
- ♦ This changes depending on the order of the reaction!
- ♦ **Just remember, the units must cancel out in the rate law equation!**
- ♦ Rate is M/t (where t is some unit of time, normally seconds), concentration is molarity

Units of k, if t is seconds

- ♦ **1st order** rate = $k[\text{A}]$
 $\text{M}/\text{s} = ? \text{M}$
- ♦ k is s^{-1} or $1/\text{s}$
- ♦ **2nd order** rate = $k[\text{A}]^2$
 $\text{M}/\text{s} = ? \text{M}^2$
- ♦ k is $\text{M}^{-1}\text{s}^{-1}$ or $1/(\text{M}\cdot\text{s})$
- ♦ **0 order** rate = k
 $\text{M}/\text{s} = ?$
- ♦ k is M/s

question

- ♦ Determine k with the correct units the following rate law
 - ♦ Rate = $k[\text{NO}]^2[\text{Cl}_2]$
- | rate | $[\text{NO}]$ | $[\text{Cl}_2]$ |
|-----------|---------------|-----------------|
| .18 M/min | .10 M | .10 M |
- ♦ $k = 180 \text{ M}^{-2}\text{min}^{-1}$ or
 - ♦ $k = 180 \text{ L}^2/\text{mol}^2 \text{ min}$

Reaction order

- ♦ The " n " variable in the expression
- ♦ A **reaction order** is a positive or negative exponent, for a reactant, for which the concentration is raised to in a rate law.
- ♦ For most problems we will deal with, it will be positive integer.

2 types of rate laws

- ♦ The **differential rate law** (often called simply the rate law) shows how the rate of reaction depends on concentration.
- ♦ The **integrated rate law** shows how the concentrations of species in the reaction depend on time.

- ♦ Because the differential and integrated rate laws for a given reaction are related in a well-defined way, the experimental determination of either of the rate laws is sufficient.
- ♦ Experimental convenience usually dictates which type of rate law is determined experimentally.

- Knowing the rate law for a reaction is important mainly because we can usually infer the individual steps involved in the reaction from the specific form of the rate law.

Determining the form of the rate law

- The first step in understanding how a given chemical reaction occurs is to determine the form of the rate law.
- We must determine experimentally the power to which each reactant concentration must be raised in the rate law.
- An exponent of "1" is referred to as first order.
- An exponent of "2" is referred to as second order.

Determining the form of a rate law



$$\text{Rate} = k[\text{N}_2\text{O}_3]^n$$

[N ₂ O ₃]	Rate (M/s)
.90 M	5.4 x 10 ⁻⁴
.45 M	2.7 x 10 ⁻⁴

- So $5.4 \times 10^{-4} = k(.90)^n$
- And $2.7 \times 10^{-4} = k(.45)^n$

Solving

- Using substitution
- $5.4 \times 10^{-4} / (.90)^n = k$
- $2.7 \times 10^{-4} = k(.45)^n$
- $2.7 \times 10^{-4} = (.45)^n 5.4 \times 10^{-4} / (.90)^n$
- $2.7 \times 10^{-4} / 5.4 \times 10^{-4} = (.45 / .90)^n$
- $.5 = .5^n$

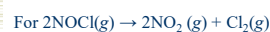
solving

- $.5 = .5^n$
- $n=1$
- You can use logarithms to solve for n, but since it is 1 it is easy to see.
- $\log(.5) = n \log(.5)$
- $n = \log(.5) / \log(.5) = 1$
- All problems should have easy numbers to work with (i.e. 1, 2, 3)

To solve for k

- Just plug your value for n into either equation
- $5.4 \times 10^{-4} \text{ M/s} = k(.90\text{M})^1$
- $2.7 \times 10^{-4} \text{ M/s} = k(.45\text{M})^1$
- Either way
- $k = 6.0 \times 10^{-4} \text{ s}^{-1}$

Determine the form of a rate law



[NOCl]	Rate (M/s)
5.0 x 10 ⁻⁴ M	1.35 x 10 ⁻⁴
1.67 x 10 ⁻⁴ M	5.0 x 10 ⁻⁶

Method of Initial Rates

- Initial rate is the instantaneous rate at $t = 0$.
- The overall reaction order is the sum of the orders for the various reactants.

Overall Reaction Order

- The sum of the exponents in the reaction rate equation.
- $\text{Rate} = k[\text{A}]^n[\text{B}]^m$
- Overall reaction order = $n + m$
- k = rate constant
- [A] = concentration of reactant A
- [B] = concentration of reactant B

Example Problem

- From the experimental data below, determine the differential rate law.
- $\text{NH}_4^+(\text{aq}) + \text{NO}_2^-(\text{aq}) \rightarrow \text{N}_2(\text{g}) + \text{H}_2\text{O}(\text{g})$

Experiment	Initial rate M/s	$[\text{NH}_4^+]$	$[\text{NO}_2^-]$
1	1.35×10^{-7}	.100 M	.0050 M
2	2.70×10^{-7}	.100 M	.010 M
3	5.40×10^{-7}	.200 M	.010 M

Solving

- Using $\text{Rate} = k[\text{A}]^n[\text{B}]^m$
- We know
- $1.35 \times 10^{-7} = k(.100)^n (.0050)^m$
- $2.70 \times 10^{-7} = k(.100)^n (.010)^m$
- $5.40 \times 10^{-7} = k(.200)^n (.010)^m$
- Now with substitution

Solving for m

- $1.35 \times 10^{-7} / (.0050)^m = k(.100)^n$
- $2.70 \times 10^{-7} = k(.100)^n (.010)^m$
- $2.70 \times 10^{-7} = (.010)^m 1.35 \times 10^{-7} / (.0050)^m$
- $2.70 \times 10^{-7} / 1.35 \times 10^{-7} = (.010 / .0050)^m$
- $2 = 2^m$
- $m = 1$

Solving for n

- $2.70 \times 10^{-7} / (.100)^n = k(.010)^m$
- $5.40 \times 10^{-7} = (.200)^n k (.010)^m$
- $5.40 \times 10^{-7} = (.200)^n 2.70 \times 10^{-7} / (.100)^n$
- $2 = 2^n$
- $n = 1$

Order of the reaction

- Order of reaction = $n + m$
- $1 + 1 = 2$
- To solve for k plug these values in
- $1.35 \times 10^{-7} \text{ M/s} = k(.100\text{M})^1 (.0050\text{M})^1$
- $2.70 \times 10^{-7} \text{ M/s} = k(.100\text{M})^1 (.010\text{M})^1$
- $k = 2.7 \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$

Example

- For the reaction below, determine the experimental rate law.
- $\text{NO}_2(\text{g}) + \text{CO}(\text{g}) \rightarrow \text{NO}(\text{g}) + \text{CO}_2(\text{g})$

Experiment	Initial Rate	Initial $[\text{NO}_2]$	Initial $[\text{CO}]$
1	0.0050	0.10 M	0.10 M
2	0.0800	0.40 M	0.10 M
3	0.0050	0.10 M	0.20 M

Another

- Determine the rate law for
- $\text{H}_2 + \text{I}_2 \rightarrow 2\text{HI}$

Experiment	Initial Rate	Initial $[\text{H}_2]$	Initial $[\text{I}_2]$
1	1.9×10^{-23}	0.0113 M	0.0011 M
2	1.1×10^{-22}	0.022 M	0.0033 M
3	9.3×10^{-23}	0.055 M	0.0011 M
4	1.9×10^{-22}	0.022 M	0.0056 M