Kinetics 15.1

Reaction Rates
The Order of Reactions
Rate Laws

Kinetics

The study of reaction rates

The rate of a reaction can be viewed 3 ways:

1) The rate of disappearance of a reactant.
2) The rate of appearance of a product.
3) The rate at which the overall reaction proceeds.

All reaction rates are found by looking at the change in concentration over a period of time.

Kinetics

A + B → D + E

1) Rate of disappearance of a single reactant

$$\text{Rate}_A = \frac{-\Delta[A]}{\Delta t}$$

The negative sign is needed, as rates are always positive values.

2) Rate of appearance of a single product

$$\text{Rate}_D = \frac{\Delta[D]}{\Delta t}$$

Kinetics

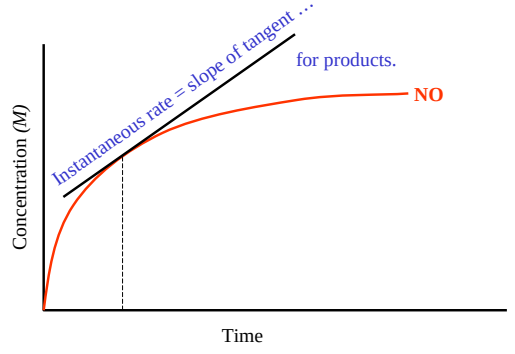
The rate at which one species appears or disappears can be used to find other rates.

aA + bB → dD + eE

$$\frac{1}{a}\times\frac{-\Delta[A]}{\Delta t} = \frac{1}{b}\times\frac{-\Delta[B]}{\Delta t} = \frac{1}{d}\times\frac{\Delta[D]}{\Delta t} = \frac{1}{e}\times\frac{\Delta[E]}{\Delta t}$$

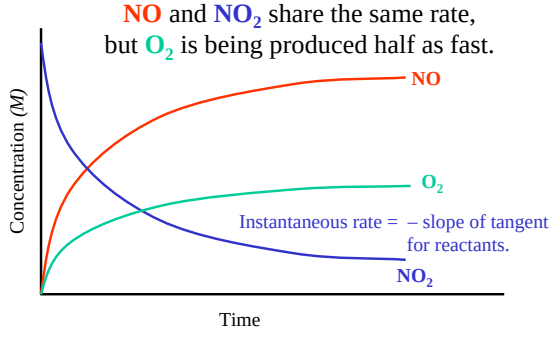
Rate_A Rate_B Rate_D Rate_E

$2\ NO_{2(g)} \rightarrow 2\ NO_{(g)} + O_{2(g)}$

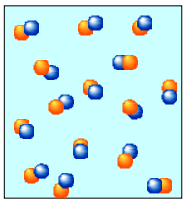


$2\ NO_{2(g)} \rightarrow 2\ NO_{(g)} + O_{2(g)}$

NO and **NO_2** share the same rate, but **O_2** is being produced half as fast.



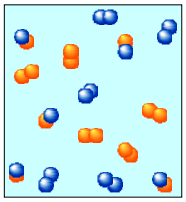
$2\ AB \rightarrow A_2 + B_2$



$t = 0.00$ s

[AB] = 15.00 *M*,

$[A_2] = 0\ M$, $[B_2] = 0\ M$



$t = 60.00$ s

[AB] = 5.00 *M*,

$[A_2] = 5.00\ M$, $[B_2] = 5.00\ M$

$2\ AB \rightarrow A_2 + B_2$

Rate of disappearance of AB

$$\text{Rate}_{AB} = \frac{-\Delta[AB]}{\Delta t} = \frac{-(5.00M - 15.00M)}{60.00\text{ s}} = \frac{-(-10.00M)}{60.00\text{ s}}$$

$$\text{Rate}_{AB} = 0.1667\ M/\text{s}$$

Rate of appearance of A_2

$$\text{Rate}_{A_2} = \frac{\Delta[A_2]}{\Delta t} = \frac{(5.00M - 0.00M)}{60.00\text{ s}} = \frac{(5.00M)}{60.00\text{ s}}$$

$$\text{Rate}_{A_2} = 0.0833\ M/\text{s}$$

or

$$\text{Rate}_{A_2} = \frac{1}{2} \times \text{Rate}_{AB} = \frac{1}{2} \times 0.1667\ M/\text{s} = 0.08335\ M/\text{s}$$

Rate Law

3) The rate of the overall reaction.

$A + B \rightarrow C + D$

Rate = k $[A]^m \bullet [B]^n$

Rate = rate of disappearance of reactants (*M*/time)

k = rate constant, specific to a certain reaction at a certain temperature.

m = reaction order in terms of A

n = reaction order in terms of B

Reaction Orders (m and n)

Reaction orders cannot be predicted from the balanced equation.

They are only found through experimental data.

Reaction orders may be:

- **»Zero Order**
- **»First Order**
- **»Second Order**

Meaning that ***m*** or ***n*** may be 0, 1, or 2.

Reaction Orders (m and n)

Zero Order Reactions

- Doubling the concentration of that species, has no affect on the reaction rate.

Rate = $k\ [A]^0$

Rate = k

Doubling [A] gives the same rate

Rate = $k\ (2[A])^0$

Rate = k

Reaction Orders (m and n)

First Order Reactions

- Doubling the concentration of that species, doubles the reaction rate.

Rate = $k\ [A]^1$

Rate = $k\ (x)^1$

Rate = $k \cdot x$

Doubling [A] doubles the rate

Rate = $k\ (2x)^1$

Rate = $2(k \cdot x)$

Reaction Orders (*m* and *n*)

Second Order Reactions

- Doubling the concentration of that species, quadruples the reaction rate.

$$\text{Rate} = k\,[A]^2$$

$$\text{Rate} = k\,(x)^2$$

$$\text{Rate} = k \cdot x^2$$

Doubling [A] quadruples the rate

$$\text{Rate} = k\,(2x)^2$$

$$\text{Rate} = 4(k \cdot x^2)$$

Overall Order for a Reaction

- To find the overall order of a reaction you simply add the exponents in the rate law.

$$\textbf{Rate} = k\,[A]^m \bullet [B]^n$$

Overall Order of the Reaction = $m + n$

Units for *k* – The Rate Constant

Order of Reaction	Basic Formula	Units for *k*
0	Rate = k	$M s^{-1}$
1	Rate = $k\,[A]$	s^{-1}
2	Rate = $k\,[A]^2$	$M^{-1}s^{-1}$
3	Rate = $k\,[A]^3$	$M^{-2}s^{-1}$

Ex1) Rate Law

Ex1) Three experiments were conducted at a specific temperature for the following reaction.

$$2\,NO_{(g)} + 2\,H_{2(g)} \rightarrow N_{2(g)} + 2\,H_2O_{(g)}$$

Experiment	$[NO]_{initial}$	$[H_2]_{initial}$	$Rate_{initial}$
1	0.20 *M*	0.30 *M*	0.0900 *M*/s
2	0.10 *M*	0.30 *M*	0.0225 *M*/s
3	0.10 *M*	0.20 *M*	0.0150 *M*/s

Find: a) The rate law.

b) The rate constant at this temperature.

c) The order for the overall reaction.

Ex1) a) Find the Rate Law

Experiment 2 to Experiment 1

$$\frac{\text{Rate}_1}{\text{Rate}_2} = \frac{k[NO]_1^n\,[H_2]_1^m}{k[NO]_2^n\,[H_2]_2^m}$$

$$\frac{0.0900\ M/s}{0.0225\ M/s} = \frac{k(0.2)^n(0.3)^m}{k(0.1)^n(0.3)^m}$$

$$4 = \frac{(0.2)^n}{(0.1)^n} = 2^n$$

[NO] doubled and $[H_2]$ stayed the same

–The rate quadruples

–2nd order for NO

***n* = 2 (second order)**

Ex1) a) Find the Rate Law (cont.)

Experiment 3 to Experiment 2

$$\frac{\text{Rate}_3}{\text{Rate}_2} = \frac{k[NO]_3^n\,[H_2]_3^m}{k[NO]_2^n\,[H_2]_2^m}$$

$$\frac{0.0150\ M/s}{0.0225\ M/s} = \frac{k(0.1)^n(0.2)^m}{k(0.1)^n(0.3)^m}$$

$$0.67 = \frac{(0.2)^m}{(0.3)^m} = 0.67^m$$

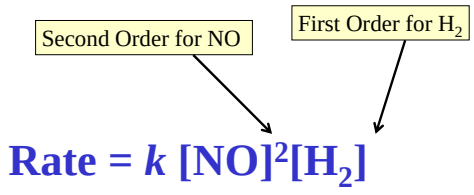
$[H_2]$ goes up by ½ and [NO] stays the same

–The rate goes up by a factor of ½

–1st order for H_2

***m* = 1 (first order)**

Ex1) a) Find the Rate Law (cont.)



Rate = k $[NO]^2[H_2]$

Ex1) b) Find the Rate Constant

Ex2) Rate Law

Ex2) Three experiments were conducted at a specific temperature for the following reaction.

$$2\ ICl + H_2 \rightarrow I_2 + HCl$$

Experiment	$[ICl]_{initial}$	$[H_2]_{initial}$	$Rate_{initial}$
1	0.20 *M*	0.20 *M*	0.0060 *M*/s
2	0.40 *M*	0.20 *M*	0.012 *M*/s
3	0.20 *M*	0.60 *M*	0.018 *M*/s

Find: a) The rate law.
b) The rate constant at this temperature.
c) The order for the overall reaction.

Ex2) a) Find the Rate Law

Ex2) a) Find the Rate Law (cont.)

Ex2) b) Find the Rate Constant