# Chemical Kinetics

## Chapter 12

Kinetics-

- the study of rates and mechanisms of chemical reactions

Rate-

- how fast a reaction proceeds
- can be measured by how fast a reactant is used up or how fast a product is formed
- rate is not constant
- it decreases with time as reactants are used up
- an equation's coefficients relate rates of consumption of reactants and production of products

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

- $NO_2$ is being consumed at the same rate that NO is being produced
- $O_2$ is being produced at ½ the rate of consumption of $NO_2$

### Mechanism

- a series of steps by which the reactants are transformed into the products

Ex. $2H_2 + O_2 \rightarrow 2H_2O$

1. $H_2 + O_2 \rightarrow 2OH$
2. $OH + H_2 \rightarrow H_2O + H$
3. $\underline{H + OH \rightarrow H_2O\quad\quad}$

$2H_2 + O_2 \rightarrow 2H_2O$

### Rate Determining Step

- the slowest step in a reactions mechanism
- this step determines how fast the reaction proceeds
- the "molecularity" of the rate determining step is reflected in the Rate Law
  (molecularity = the number & type of particles that are reactants in the slow step)
- the reaction can go no faster than its slow step

### Rate Law

- an equation that shows what type of particles are the reactants in the rate determining step (the slow step)
- it must be determined by experiment
- the reaction is carried out a number of times varying the concentration of one reactant at a time

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

| Experiment | Initial [ ]'s (m) | |
|---|---|---|

|  | NO | $H_2$ | Initial Rate $\left(\frac{atm}{\min}\right)$ |
|---|---|---|---|
| 1 | .006 | .001 | .025 |
| 2 | .006 | .002 | .050 |
| 3 | .006 | .003 | .075 |
| 4 | .001 | .009 | .0063 |
| 5 | .002 | .009 | .025 |
| 6 | .003 | .009 | .056 |

Results

- for $H_2$: if the $[H_2]$ doubles, the rate of the reaction doubles
    - the rate of the reaction is $\propto [H_2]^1$
- for NO: if the [NO] doubles, the rate of the reaction quadruples
    - the rate of the reaction is $\propto [NO]^2$
- for each substance, the exponent ih how many of that particle participate in the rate determining step
- the exponent is referred to as the "Order of the reactant"
- $H_2$ is a 1st order reactant
- NO is a 2nd order reactant

So: Rate $\propto [H_2]\,[NO]^2$

- to make a proportion an equality you need a proportionality constant, K
    - K= the rate constant
        - characteristic for a specific reaction but varies with temperature

So:

Rate = K $[H_2]\,[NO]^2$

is the rate law for this reaction

- this is a 3rd order reaction
- 3 particles must collide as reactants in the rate determining step

  ($1H_2$ + 2NO's)

In general:

$2S + 3B \rightarrow C + 4D$

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

**n & m must be determined experimentally**

**Ex. 12.1**

$BrO_3^-(aq) + 5Br^-(aq) + 6H^+(aq) \rightarrow 3Br_2(l) + 3H_2O$

|  | $[BrO_3^-]$ | $[Br^-]$ | $[H^+]$ | Init. Rate (mol/L•s) |
|---|---|---|---|---|
| 1 | 0.10 | 0.10 | 0.10 | $8.0 \times 10^{-4}$ |

| | | | | |
|---|---|---|---|---|
| 2 | 0.20 | 0.10 | 0.10 | 1.6 X $10^{-3}$ |
| 3 | 0.20 | 0.20 | 0.10 | 3.2 X $10^{-3}$ |
| 4 | 0.10 | 0.10 | 0.20 | 3.2 X $10^{-3}$ |

Calculate the rate law and the rate constant.

## Writing a Mechanism

1. Determine the Rate Law
2. Write the rate determining step based on the rate law
3. Write other steps so that the sum of all the steps yields the overall equation
4. Cancel all duplication

**Ex. 12.6**

$2NO_2(g) + F_2(g) \rightarrow 2NO_2F(g)$
and Rate = $k[NO_2][F_2]$

Ex. $2NO(g) + Cl_2(g) \rightarrow 2NOCl$
and rate = $k\,[NO][Cl_2]$
Speculate on a mechanism for this reaction.

Ex. $2H_2 + O_2 \rightarrow 2H_2O$
If, for this reaction, Rate = $k\,[OH][H]$, speculate on a mechanism

Ex. A + 2B + C → AB + BC

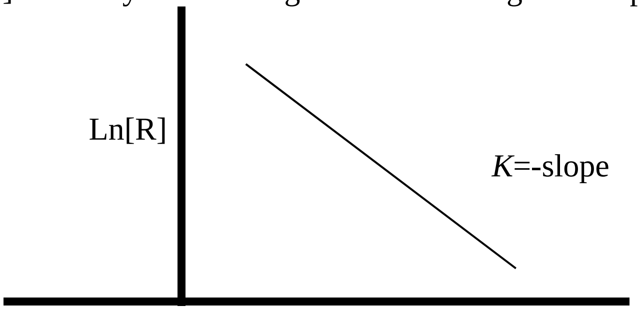
| Experiment | [A], M | [B], M | [C], M | Rate (mol/l•s) |
|---|---|---|---|---|
| 1 | 1.00 | 1.00 | 2.00 | 1.00 |
| 2 | 2.00 | 1.00 | 2.00 | 2.00 |
| 3 | 2.00 | 2.00 | 2.00 | 8.00 |
| 4 | 2.00 | 2.00 | 4.00 | 8.00 |

a) Rate Law =
b) *k* =
c) If [A] = 1.0M, [B] = 2.0M & C= 3.0M, then Rate =
d) Speculate on a mechanism for this reaction

## Order of a Reactant from Graphing

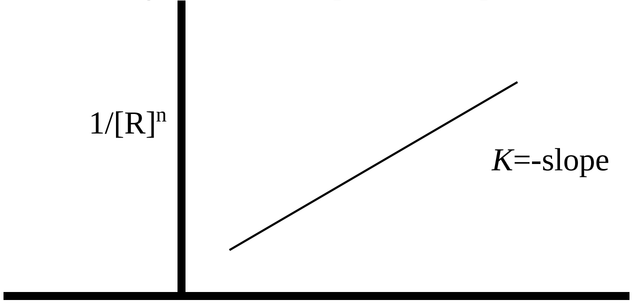
### 1st Order Reactant

- A graph of ln[R] vs time yields a straight line with a negative slope



**<u>Orders Greater than 1</u>**

- graph $1/[r]^h$ vs. time where n=1, 2, 3 etc.
- one graph will yield a straight line with a positive slope.



(trial and error: tedious)

- For the graph that yields a straight line with a positive slope:
  - n + 1 = the order of the reactant
  - *k* = the slope of the straight line

**<u>Half Life ($t_{1/2}$)</u>**

- The time required for a reactant to reach ½ of its original concentration.
  - (use up ½ of what you started with)
- For a 1st order reaction (only 1 reactant particle
  - $t_{1/2}$ is a constant amount of time
  - $t_{1/2}$ does not depend on the initial concentration of the reactant

$$\boxed{t_{1/2} = .693/k}$$

Ex. 12.4

A certain first order reaction has a half-life of 20.0 min.

a) Calculate the rate constant, *k*, for this reaction.

b) How much time is required for this reaction to be 75% complete?

- $t_{1/2}$ is **<u>not</u>** constant for other order reactions
  - 2nd order reaction: $t_{1/2} = 1/k[R]$

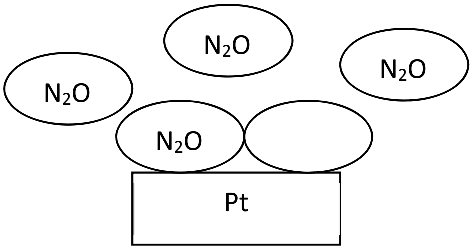
  - $t_{1/2}$ depends on *k* & R
  - each successive ½ life would be double the previous one because the [R] is half of what it was.

**Zero Order Reaction**

- occurs in a heterogeneous system
- reaction can only occur where particles can come in contact
- rate is independent of [R]
  - Rate = $k[R]^0 = k$

Ex. $2N_2O(g) \rightarrow 2N_2(g) + O_2(g)$ on a hot platinum surface (Pt acts as catalyst)

  - Only molecules on the Pt can react
  - Increasing $[N_2O]$ will not cause more reaction to occur

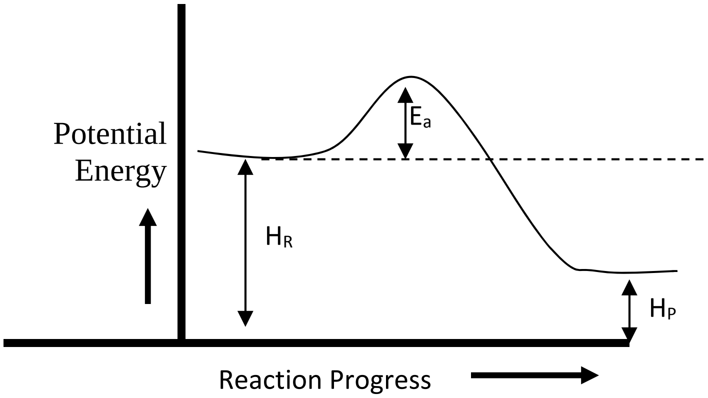


**Collision Model**

- Particles must collide to react
- The more particles that must collide in a step, the less likely that the step will occur.
- For a collision to produce the desired change it must
  - have the required activation energy
  - have the correct particle orientation
  -

***1. Activation Energy***

- Amount of energy needed to produce a chemical change
- Energy needed to break bonds in the reacting molecules
- Allows particles to form the "activated complex" (a transition state)



If the specific rate constant is known at two different temperatures, $E_a$ (activation energy) can be calculate:

$$\ln\left(\frac{k_1}{k_2}\right) = \frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_2}\right)$$

R = 8.31 j/mol•k

Ex. 12.9

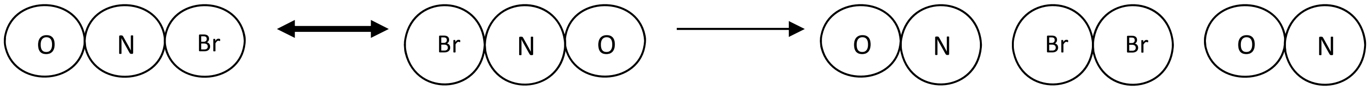
$CH_4(g) + 2S_2(g) \rightarrow CS_2(g) + 2H_2S(g)$

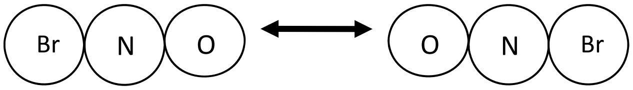
$k_1 = 1.1$ L/mol•s  $T_1 = 550°C = 823K$

$k_2 = 6.4$ L/mol•s  $T_2 = 625°C = 898K$  $R = 8.31$ j/mol•K

2. ***Correct particle orientation***
   - if specific atoms are to bond, those atoms must collide

Ex. $2BrNO \rightarrow 2NO + Br_2$





**NO REACTION**

- Factors Affecting Rate of Reaction
  - Concentration of Reactants
    - (molecularity of rate determining step)
  - Temperature
    - increasing temperature, increases the rate of chemical reaction
    - at higher temperature, the collisions are more energetic
    - a greater percentage of the collisions have the required activation energy
    - in the rate law, the value of *k* increases

3. ***Catalysis***
   - Catalyst – a substance that speeds up a reaction without being consumed
     - it changes the mechanism to one that requires less activation energy (more "energetically favorable')
     - with lower energy requirement a larger percentage of collisions are effective collisions
     - the catalyst gets used up in one step, and reformed in a subsequent step

Ex.

$SO_2(g) + \frac{1}{2} O_2(g) \rightarrow SO_3(g)$

- $NO_2$ catalyzes this reaction

1 $SO_2(g) + NO_2(g) \rightarrow SO_3(g) + NO(g)$ used up

2 $NO(g) + \frac{1}{2} O_2(g) \rightarrow NO_2(g)$

Ex.

$$2O_3 \rightarrow 3O_2$$

$$\begin{array}{ll} 1 & Cl + O_3 \rightarrow ClO + O_2 \\ 2 & ClO \rightarrow Cl + O \\ 3 & O + O_3 \rightarrow 2O_2 \\ \hline & 2O_3 \rightarrow 3O_2 \end{array}$$