# CHEMICAL KINETICS

Chemical kinetics is the study of the rate at which reactions occur.

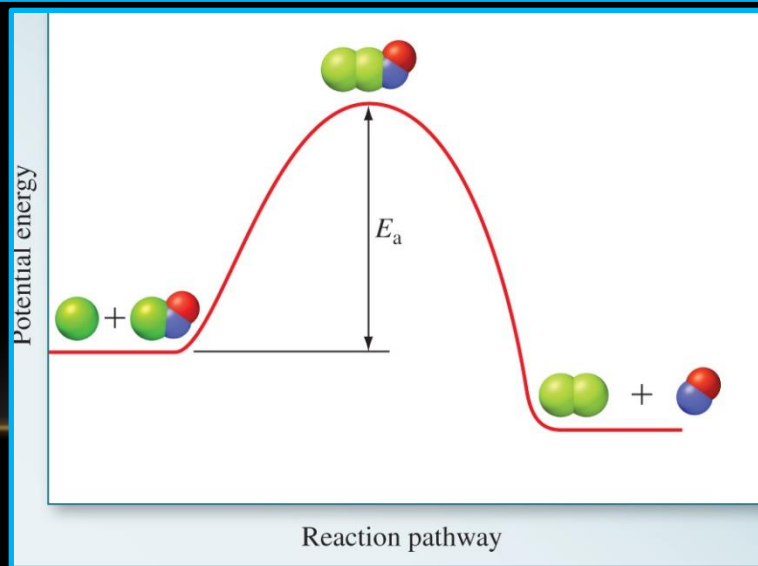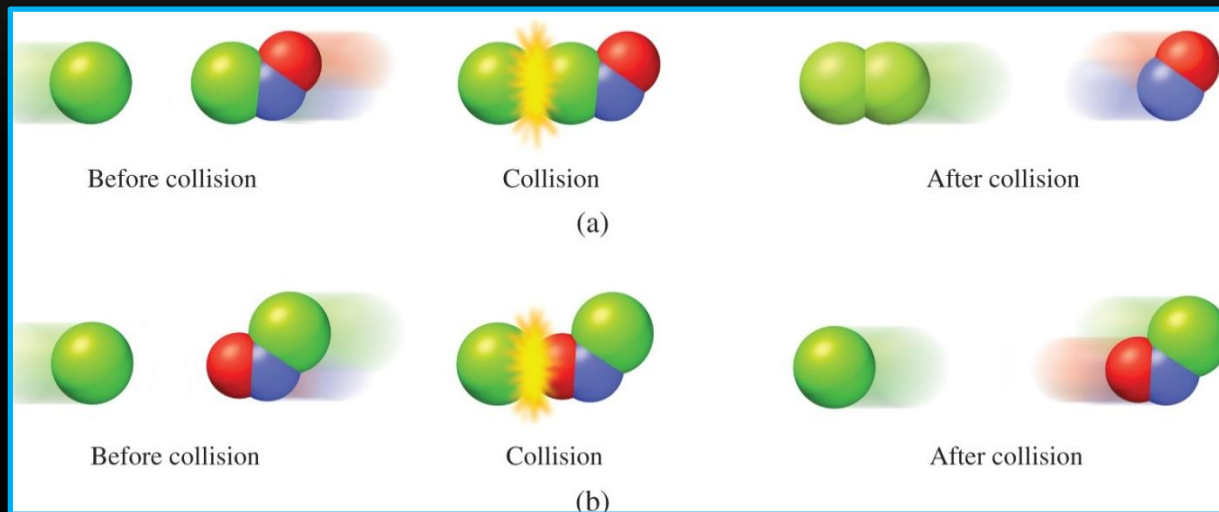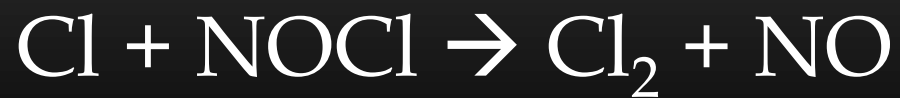In order for a chemical reaction to occur, several things have to happen at once:

The reactants must collide

They must have enough energy to initiate the reaction

They must hit each other with the correct orientation

This is called Collision Theory.

# COLLISION THEORY

# Cl + NOCl → Cl$_2$ + NO



Before collision     Collision     After collision

(a)

Before collision     Collision     After collision

(b)
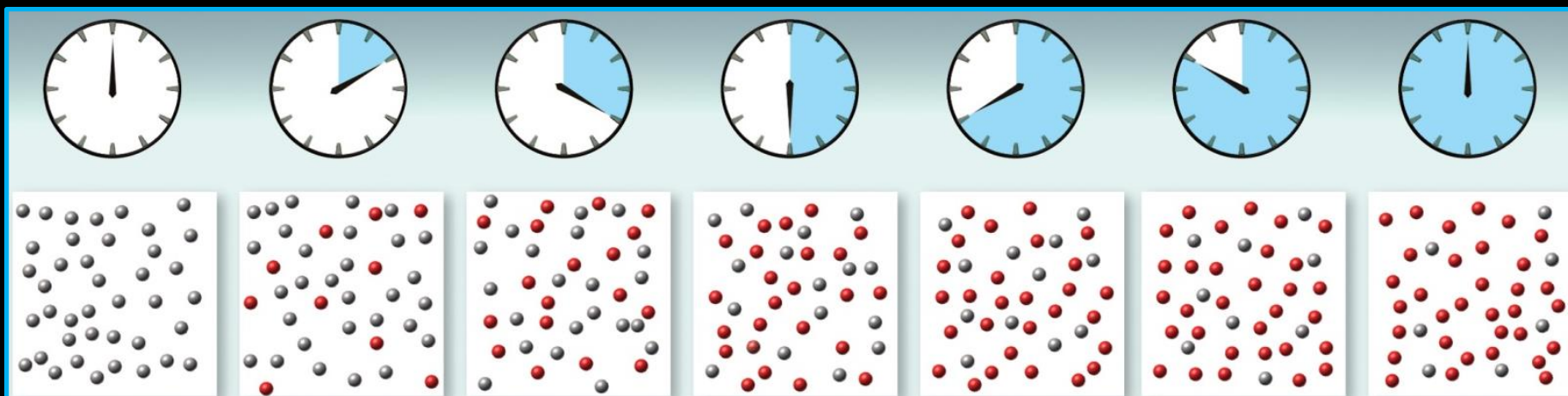
Potential energy

$E_a$

+

+

Reaction pathway
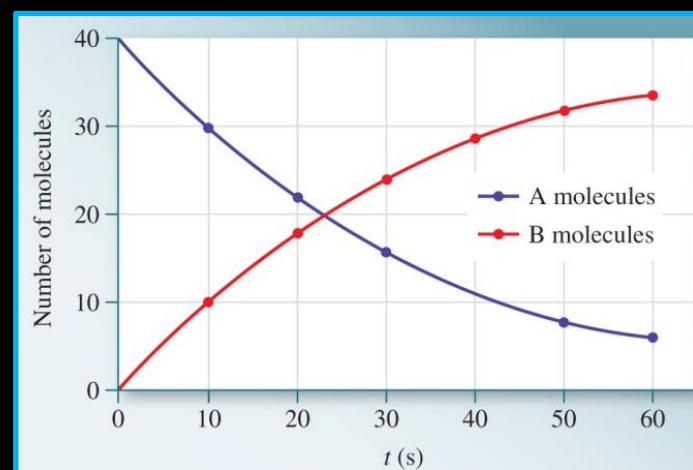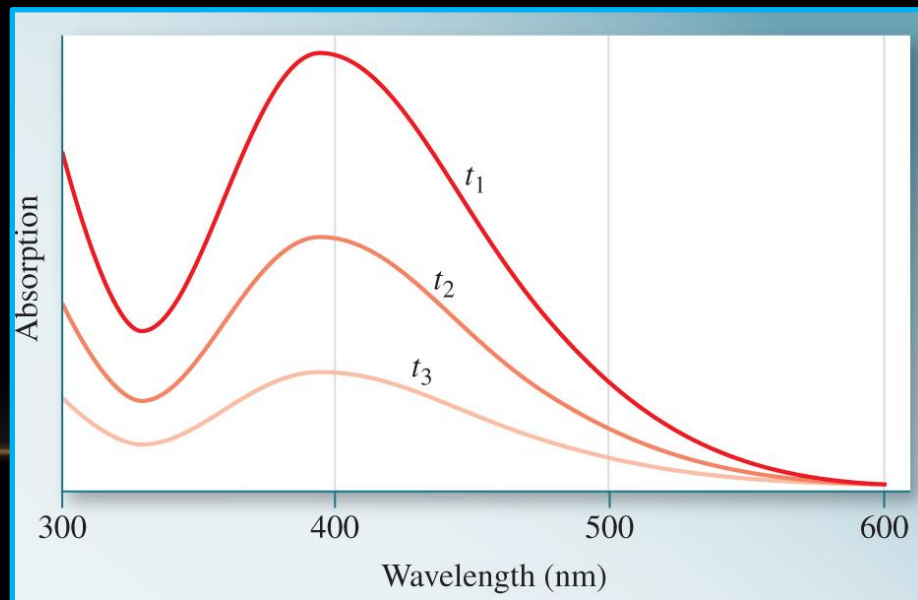
# REACTION RATES

# MEASURING THE PROGRESS OF A REACTION

We can monitor either the decrease in concentration of reactants, or the increase in the concentration of products to follow the progress of a reaction.

For the reaction A → B:

$$\text{Average rate} = -\frac{\Delta[A]}{\Delta t} = \frac{\Delta[B]}{\Delta t}$$

$$Br_2(aq) + HCO_2H(aq) \rightarrow 2Br^-(aq) + 2H^+(aq) + CO_2(g)$$

$$Br_2(aq) + HCO_2H(aq) \rightarrow 2Br^-(aq) + 2H^+(aq) + CO_2(g)$$

| Time (s) | [Br$_2$] ($M$) | Rate ($M$/s) |
|---|---|---|
| 0.0 | 0.0120 | $4.20 \times 10^{-5}$ |
| 50.0 | 0.0101 | $3.52 \times 10^{-5}$ |
| 100.0 | 0.00846 | $2.96 \times 10^{-5}$ |
| 150.0 | 0.00710 | $2.49 \times 10^{-5}$ |
| 200.0 | 0.00596 | $2.09 \times 10^{-5}$ |
| 250.0 | 0.00500 | $1.75 \times 10^{-5}$ |
| 300.0 | 0.00420 | $1.48 \times 10^{-5}$ |
| 350.0 | 0.00353 | $1.23 \times 10^{-5}$ |
| 400.0 | 0.00296 | $1.04 \times 10^{-5}$ |

Rates of reaction for bromine with formic acid.
To find the average rate over a time interval, take
the difference in concentrations over the difference in time.
Because bromine is a reactant, take the opposite sign.

# INSTANTANEOUS RATE

Rate at 100 s:
$2.96 \times 10^{-5}$ M/s

Rate at 200 s:
$2.09 \times 10^{-5}$ M/s

Rate at 300 s:
$1.48 \times 10^{-5}$ M/s

[Br$_2$] (M)

$t$ (s)
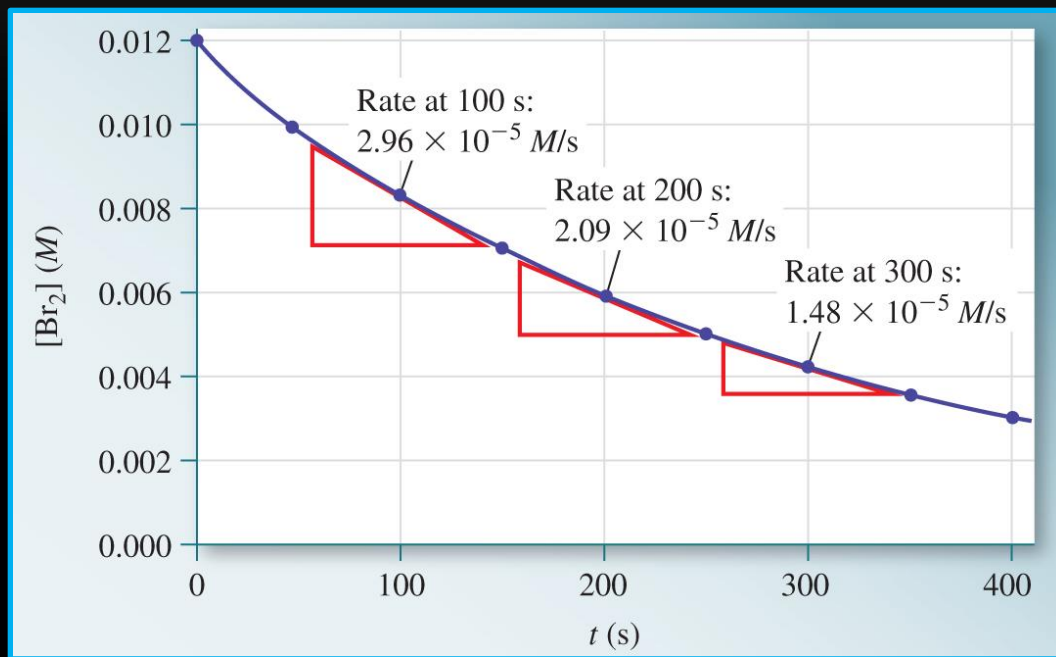
The instantaneous rate is the slope of the tangent to the curve at any time.
Note how the rate decreases as time increases. This is because the [Br$_2$] decreases.

# INSTANTANEOUS RATE

| Time (s) | [Br$_2$] (M) | Rate (M/s) |
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Comparing the [Br$_2$] at t=100 and t=350 to the rate at those times we see that the ratio of the concentrations is equal to the ratio of the rates. This means that the rate is directly proportional to the [Br$_2$]:

$$\text{rate} = k[Br_2]$$

# INSTANTANEOUS RATE

| Time (s) | [Br$_2$] (M) | Rate (M/s) |
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**rate = k[Br$_2$]**

If we rearrange this to solve for k, and plug in any two values for rate and [Br$_2$], we get the same number (within experimental error) for any combination of the two: $3.5 \times 10^{-3}$/s.  Thus the rate constant, k, is independent of [Br$_2$].  It does depend on temperature though.

# USING A GAS TO MONITOR THE RATE

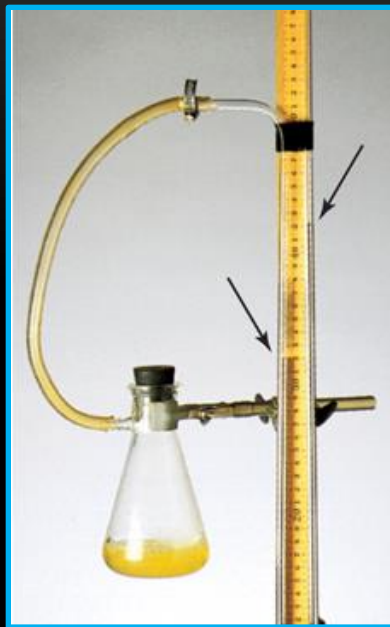For the reaction $2H_2O_2(aq) \rightarrow 2H_2O(l) + O_2(g)$ we can measure the progress of the reaction by measuring the pressure of $O_2$ produced.

# USING A GAS TO MONITOR THE RATE

$2H_2O_2(aq) \rightarrow 2H_2O(l) + O_2(g)$

$$P_{O_2} = \frac{nRT}{V} \Rightarrow [O_2] = \frac{1}{RT}P_{O_2}$$



$$\text{So rate} = \frac{\Delta[O_2]}{\Delta t} = \frac{1}{RT}\frac{\Delta P_{O_2}}{\Delta t}$$

# STOICHIOMETRY AND REACTION RATE

For the reaction A $\rightarrow$ 2B, Average rate $= -\frac{\Delta[A]}{\Delta t} = \frac{1}{2}\frac{\Delta[B]}{\Delta t}$ .

In general, for the reaction aA + bB $\rightarrow$ cC + dD,

$$\text{Average rate} = -\frac{1}{a}\frac{\Delta[A]}{\Delta t} = -\frac{1}{b}\frac{\Delta[B]}{\Delta t} = \frac{1}{c}\frac{\Delta[C]}{\Delta t} = \frac{1}{d}\frac{\Delta[D]}{\Delta t}$$

**(MEMORIZE)**

# EXAMPLE

For the reaction $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$.  At a given time the hydrogen is reacting at a rate of 0.0432 M/s.  At what rate is ammonia formed?  At what rate is hydrogen reacting?

$NH_3$: 0.0864 M/s

$H_2$: -0.130 M/s

# REACTION RATE AND REACT AND REACTANT CONCENTRATION

# THE RATE LAW

The rate law for a reaction relates the rate to the concentrations. For the general reaction

$$aA + bB \rightarrow cC + dD$$

The rate law is

$$Rate = k[A]^x[B]^y$$

**(MEMORIZE)**

Here x and y are determined experimentally.

# EXPERIMENTAL DETERMINATION OF THE RATE LAW

Consider this reaction:

$$F_2(g) + 2ClO_2(g) \rightarrow 2FClO_2(g) \qquad Rate = k[F_2]^x[ClO_2]^y$$

The following table gives initial rates for the reaction
For different initial concentrations of the reactants.

| Experiment | $[F_2]$ (M) | $[ClO_2]$ (M) | Initial rate (M/s) |
|:---:|:---:|:---:|:---:|
| 1 | 0.10 | 0.010 | $1.2 \times 10^{-3}$ |
| 2 | 0.10 | 0.040 | $4.8 \times 10^{-3}$ |
| 3 | 0.20 | 0.010 | $2.4 \times 10^{-3}$ |

We can use this data to determine the exponents x and y in the rate law, and thus the rate law.

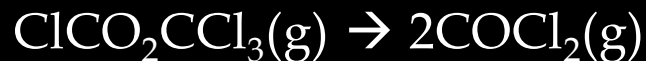$$x = 1, y = 1 \qquad Rate = k[F_2][ClO_2]$$

# EXPERIMENTAL DETERMINATION OF THE RATE LAW

Knowing the rate law, we can use the data from any of the experiments to find the rate constant.

$$k = \frac{rate}{[\text{F}_2][\text{ClO}_2]} = \frac{4.8 \times 10^{-3}}{(0.10\ M)(0.040\ M)} = 1.2/M \cdot s$$

# EXAMPLE

Use the following data (P is the total pressure), collected at 312 ºC in a constant volume container, to determine the order of reaction and rate constant for the reaction studied:

$$ClCO_2CCl_3(g) \rightarrow 2COCl_2(g)$$

| Time(s) | P (mmHg) |
|---------|----------|
| 0 | 15.76 |
| 181 | 18.88 |
| 513 | 22.79 |
| 1164 | 27.08 |

1st order; k= 0.001s$^{-1}$

# TIME AND CONCENTRATION

# FIRST ORDER REACTIONS

For the reaction A → products, if the reaction is first order then:

$$\text{rate} = k[A] = -\frac{\Delta[A]}{\Delta t}$$

For example, for the reaction $2N_2O_5(g) → 4NO_2(g) + O_2(g)$

$$\text{rate} = k[N_2O_5] = -\frac{\Delta[N_2O_5]}{\Delta t}$$

Using calculus, if we rearrange and integrate we find that:

$$ln\frac{[A]_t}{[A]_0} = -kt$$

or

$$ln[A]_t = -kt + [A]_0$$

An equation of a straight line where the slope is $-k$.

(MEMORIZE)

# EXAMPLE

The following reaction is first order in $H_2O_2$. Given that the starting concentration of $H_2O_2$ is 0.9946 **M**, what will be the concentration of $H_2O_2$ after 1 hour and 45 minutes? How long will it take for the concentration to reach 0.500 M? The rate constant for this reaction at 20. ºC (the temperature this reaction is occurring at) is 1.79 x 10$^{-5}$ s$^{-1}$.

$$2H_2O_2(aq) \rightarrow 2H_2(l) + O_2(g)$$
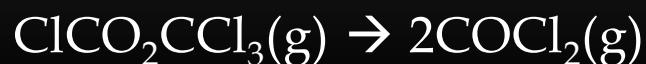
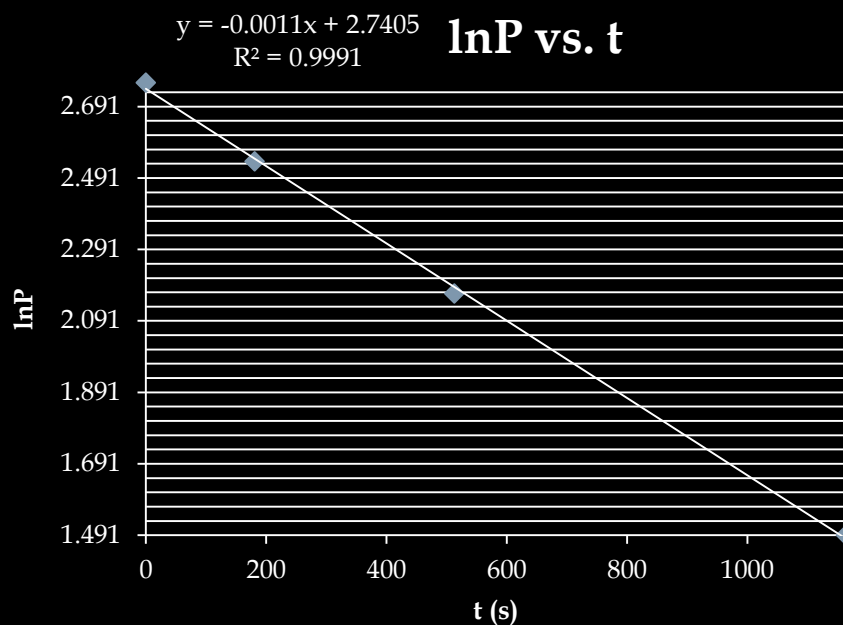$$[H_2O_2]_{6.30 \times 10^3 s} = 0.889M$$

About 11 hours

# EXAMPLE

Use the following data, collected at 312 °C in a constant volume container, to determine the order of reaction and rate constant for the reaction studied:

$$ClCO_2CCl_3(g) \rightarrow 2COCl_2(g)$$

| Time(s) | $P_{ClCO2CCl3}$ (mmHg) |
|---------|------------------------|
| 0       | 15.76                  |
| 181     | 12.64                  |
| 513     | 8.73                   |
| 1164    | 4.44                   |

| Time(s) | lnP    |
|---------|--------|
| 0       | 2.7575 |
| 181     | 2.5369 |
| 513     | 2.167  |
| 1164    | 1.491  |



lnP vs. t

y = -0.0011x + 2.7405
R² = 0.9991

1$^{st}$ order since plot of lnP v. t is linear.
k = slope = 0.001s$^{-1}$

# THE HALF-LIFE ($t_{1/2}$)

The time it takes for the concentration of a reactant to drop to ½ of it's original value.  For a first order reaction:

$$t_{1/2} = \frac{ln2}{k} = \frac{0.6931}{k}$$

This also applies to the first order decay of radioactive isotopes.

# EXAMPLE

The following reaction is first order in $H_2O_2$. What is the half-life, in hours, for this reaction? The rate constant for this reaction at 20. $^oC$ (the temperature this reaction is occurring at) is $1.79 \times 10^{-5}$ $s^{-1}$.

$$2H_2O_2(aq) \rightarrow 2H_2(l) + O_2(g)$$

**10.8 hours**

# SECOND-ORDER REACTIONS

For the reaction A → products, if the reaction is second order then:

$$\text{rate} = k[A]^2 = -\frac{\Delta[A]}{\Delta t}$$

Using calculus, if we rearrange and integrate we find that:

$$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$$

An equation of a straight line where the slope is $k$.

and

$$t_{1/2} = \frac{1}{k[A]_0}$$

Unlike first order reactions, the $t_{1/2}$ depends on the initial concentration. Finding the $t_{1/2}$ at different initial concentrations is one way to distinguish between first and second order reactions.

# EXAMPLE

The rate constant for the second order reaction

$$2NO_2(g) \rightarrow 2NO(g) + O_2(g)$$

Is 0.491 /M·s at 250 °C.  Starting with a concentration of 0.592 M, calculate the concentration of $NO_2$ after 35 s.  Calculate the half life when $[NO_2]_0$ is 0.0984 M.

$[NO_2] =$  0.053 M after 35 s
$t_{1/2} = 20.7$ s

# MEMORIZE THESE

| Order | Rate law | Integrated rate law | Half-Life |
|-------|----------|---------------------|-----------|
| 0 | $\text{rate} = k$ | $[A]_t = -kt + [A]_0$ | $\dfrac{[A]_0}{2k}$ |
| 1 | $\text{rate} = k[A]$ | $\ln \dfrac{[A]_t}{[A]_0} = -kt$ | $\dfrac{0.693}{k}$ |
| 2 | $\text{rate} = k[A]^2$ | $\dfrac{1}{[A]_t} = kt + \dfrac{1}{[A]_0}$ | $\dfrac{1}{k[A]_0}$ |

# TEMPERATURE AND RATE OF REACTION

# THE ARRHENIUS EQUATION

$$k = Ae^{-E_a/RT}$$

Here $A$ is called the frequency factor and represents the frequency with which the molecules collide. $E_a$ is the activation energy in J/mol, R is the gas constant in the form 8.314 J/K·mol and T is the temperature in K.

From this we get: $\ln k = \left(-\frac{E_a}{R}\right)\left(\frac{1}{T}\right) + \ln A$ an equation for a straight line with the slope being $-\frac{E_a}{R}$.

# ANOTHER USEFUL FORM OF THE ARRHENIUS EQUATION

$$\ln\frac{k_1}{k_2} = \frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

This lets us calculate the rate constant at a new temperature if we know it at one temperature and the activation energy.

Also, if we know the rate constant at two different temperatures we can find the activation energy.

# EXAMPLE

Calculate the rate constant at 159 ºC for a reaction that has a rate constant of 4.94 x 10$^{-3}$ at 101 ºC and an activation energy of 88.5 kJ/mol.

$$k = 0.228 \text{ s}^{-1}$$

# REACTION MECHANISMS

# REACTION MECHANISM VS. ELEMENTARY STEPS

Many chemical equations we've seen so far are not as simple as they appear, but rather are a series of elementary reactions that add up to the chemical equation we see.

An elementary reaction can be unimolecular, bimolecular, or termolecular.

The reaction order for each reactant in an elementary reaction is equal to its stoichiometric coefficient in the chemical equation for that step.

# THE RATE-DETERMINING STEP

When there is more than one elementary step for a chemical reaction, the slowest step determines the overall rate, and thus the rate law is that of the slowest step, called the rate-determining step.

The sum of the elementary steps is the overall balanced equation.

# EXAMPLE

The reaction between $NO_2$ and $CO$ to produce $NO$ and $CO_2$ probably occurs in two steps:

$$NO_2 + NO_2 \rightarrow NO + NO_3 \quad (k_1)$$

$$NO_3 + CO \rightarrow NO_2 + CO_2 \quad (k_2)$$

The experimental rate law is rate = $k[NO_2]^2$. Write the equation for the overall reaction. Which species are intermediates? Which is the RDS?

# FAST FIRST STEPS

For the reaction $2NO(g) + Cl_2(g) \rightarrow 2NOCl(g)$ the mechanism is thought to be:

Step 1: $NO(g) + Cl_2(g) \rightarrow NOCl_2(g)$ (fast, $k_1$)

Step 2: $NOCl_2(g) + NO(g) \rightarrow 2NOCl(g)$ (slow, $k_2$)

And the rate law is experimentally known to be rate = $k[NO]^2[Cl_2]$.

The rate law based on the slow step is rate = $k_2[NOCl_2][NO]$. This is correct, but involves an intermediate. Because the first step is faster than the second, an equilibrium situation develops:

$$NO(g) + Cl_2(g) \xleftrightarrow{\quad k_1 \quad} NOCl_2(g)$$

$rate_{forward} = k_1[NO][Cl_2] = rate_{reverse} = {}^k k_{-1}[NOCl_2]$. If we solve for $[NOCl_2]$ we get: $[NOCl_2] = \frac{k_1}{k_{-1}}[NO][Cl_2]$ and if we substitute into the rate law $k_2[NOCl_2][NO]$ we get:

$$rate = k_2[NOCl_2][NO] = k_2 \frac{k_1}{k_{-1}}[NO]^2[Cl_2] = k[NO]^2[Cl_2]$$

# CATALYSIS

# A CATALYST:

Lowers the activation barrier thus increasing the rate, but is not consumed in the overall reaction.

There are three types of catalysis: heterogeneous, homogeneous, and enzyme.