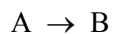


Chemical Kinetics

Reaction Rates:

Reaction Rate: The change in the concentration of a reactant or a product with time (M/s).

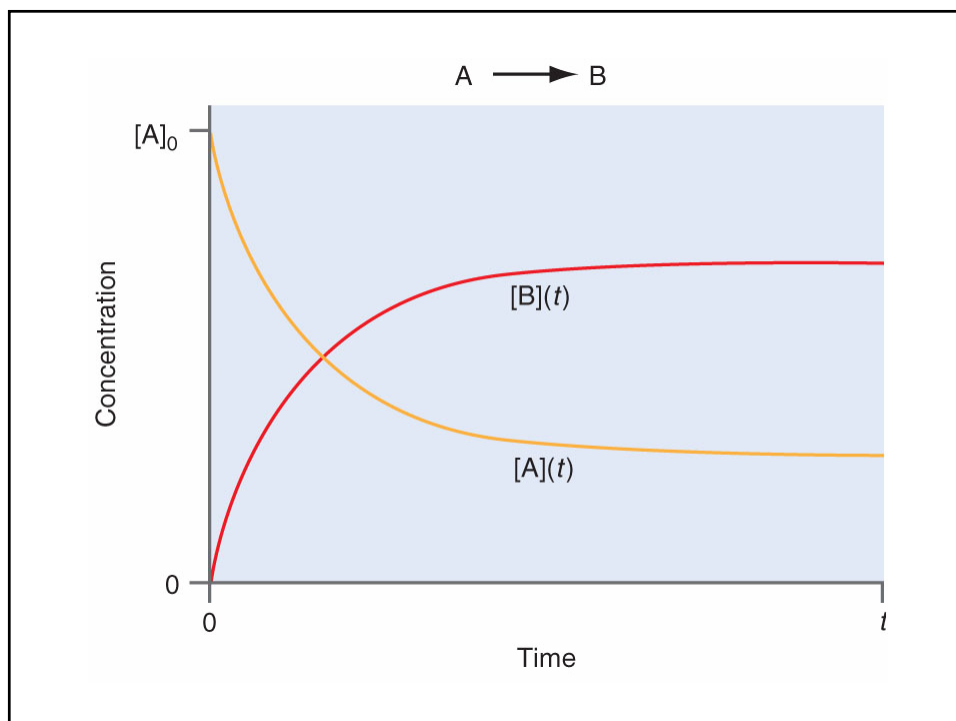
Reactant \rightarrow Products



$$\text{Average rate} = \frac{\text{change in number of moles of B}}{\text{change in time}}$$

$$= \frac{\Delta(\text{moles of B})}{\Delta t} = \frac{\Delta[B]}{\Delta t}$$

Since reactants go away with time: $\text{Rate} = -\frac{\Delta[A]}{\Delta t}$



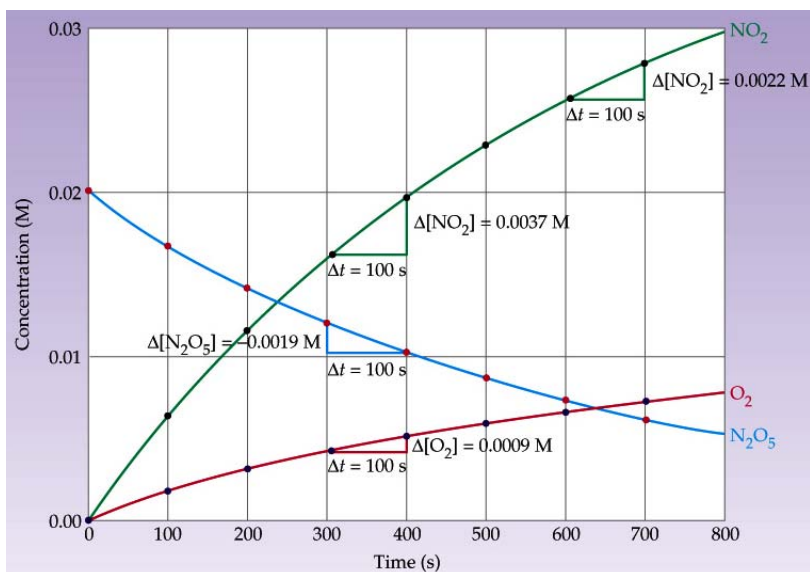
Consider the decomposition of N_2O_5 to give NO_2 and O_2 :



Time (s)	Concentration (M)		
	N_2O_5	NO_2	O_2
0	0.0200	0	0
100	0.0169	0.0063	0.0016
200	0.0142	0.0115	0.0029
300	0.0120	0.0160	0.0040
400	0.0101	0.0197	0.0049
500	0.0086	0.0229	0.0057
600	0.0072	0.0256	0.0064
700	0.0061	0.0278	0.0070

reactants
decrease with
time

products
increase with
time



From the graph looking at t = 300 to 400 s

$$\text{Rate O}_2 = \frac{0.0009\text{M}}{100\text{s}} = 9 \times 10^{-6} \text{Ms}^{-1}$$

Why do they differ?

$$\text{Rate NO}_2 = \frac{0.0037\text{M}}{100\text{s}} = 3.7 \times 10^{-5} \text{Ms}^{-1}$$

Recall:

$$\text{Rate N}_2\text{O}_5 = \frac{0.0019\text{M}}{100\text{s}} = 1.9 \times 10^{-5} \text{Ms}^{-1}$$



To compare the rates one must account for the *stoichiometry*.

$$\text{Rate O}_2 = \frac{1}{1} \times 9 \times 10^{-6} \text{Ms}^{-1} = 9 \times 10^{-6} \text{Ms}^{-1}$$

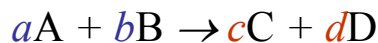
$$\text{Rate NO}_2 = \frac{1}{4} \times 3.7 \times 10^{-5} \text{Ms}^{-1} = 9.2 \times 10^{-6} \text{Ms}^{-1}$$

Now they agree!

$$\text{Rate N}_2\text{O}_5 = \frac{1}{2} \times 1.9 \times 10^{-5} \text{Ms}^{-1} = 9.5 \times 10^{-6} \text{Ms}^{-1}$$

Reaction Rate and Stoichiometry

In general for the reaction:



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

Rate Law & Reaction Order

The reaction *rate law expression* relates the rate of a reaction to the concentrations of the reactants.

Each concentration is expressed with an order (exponent).

The rate constant converts the concentration expression into the correct units of rate (Ms^{-1}). (*It also has deeper significance, which will be discussed later*)

For the general reaction: $aA + bB \rightarrow cC + dD$

$$\text{Rate} = k [A]^x [B]^y$$

x and y are the reactant orders determined from experiment.

x and y are **NOT** the stoichiometric coefficients.

Relationship between Rate Law, Order, and the Rate Constant, k^*

Rate Law	Order	Units of k
Rate = k	Zero	M s^{-1}
Rate = $k[A]$	First order with respect to A First order overall	s^{-1}
Rate = $k[A]^2$	Second order with respect to A Second order overall	$\text{M}^{-1} \text{s}^{-1}$
Rate = $k[A][B]$	First order with respect to A First order with respect to B Second order overall	$\text{M}^{-1} \text{s}^{-1}$
Rate = $k[A][B][C]$	First order with respect to A First order with respect to B First order with respect to C Third order overall	$\text{M}^{-2} \text{s}^{-1}$

*In the units of k , M represents mol L^{-1} or moles per liter.

The **Overall Order** of a reaction is the sum of the individual orders:

$$\text{Rate (Ms}^{-1}\text{)} = k[\text{A}][\text{B}]^{1/2}[\text{C}]^2$$

Overall order: $1 + \frac{1}{2} + 2 = 3.5 = \frac{7}{2}$

or ***seven-halves order***

note: when the order of a reaction is 1 (first order) no exponent is written.

Units for the rate constant:

The units of a rate constant will change depending upon the overall order.

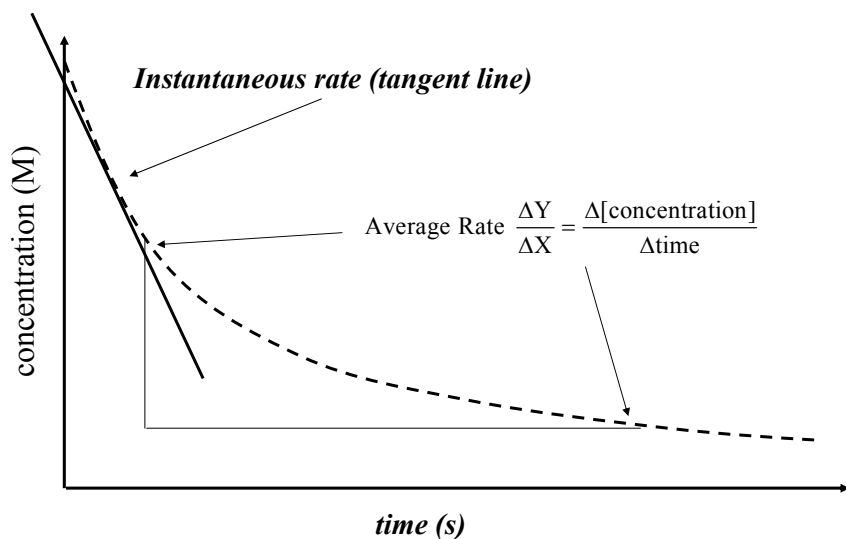
The units of rate are always M/s or Ms⁻¹

To find the units of a rate constant for a particular rate law, simply divide the units of rate by the units of molarity in the concentration term of the rate law.

$$\text{Rate (Ms}^{-1}\text{)} = k[\text{A}] \quad 1^{\text{st}} \text{ order}$$

$$k(\text{units}) = \frac{\text{Ms}^{-1}}{\text{M}} = \text{s}^{-1}$$

Reaction Rates



Rules of logarithms

$$\log(1) = 0$$

$$\ln(1) = 0$$

$$\log(10) = 1$$

$$\ln(e) = 1$$

$$\log(100) = 2$$

$$\ln(e^x) = x$$

$$\log(10^x) = x$$

$$\log A^x = x \log A$$

$$\ln A^x = x \ln A$$

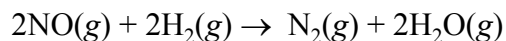
$$\log\left(\frac{A^x}{B^x}\right) = \log\left(\frac{A}{B}\right)^x = x \log\left(\frac{A}{B}\right)$$

$$\log(AB) = \log A + \log B$$

$$\log\left(\frac{A}{B}\right) = \log A - \log B$$

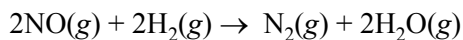
Determining Reaction Order: *The Method of Initial Rates*

The reaction of nitric oxide with hydrogen at 1280°C is:



From the following data, determine the rate law and rate constant.

Run	[NO] _o (M)	[H ₂] _o (M)	Initial Rate (M/min)
1	0.0100	0.0100	0.00600
2	0.0200	0.0300	0.144
3	0.0100	0.0200	0.0120



The rate law for the reaction is given by:

$$\text{Rate}(\text{M}/\text{min}) = k [\text{NO}]^x [\text{H}_2]^y$$

Taking the ratio of the rates of runs 3 and 1 one finds:

$$\frac{\text{Rate}(3)}{\text{Rate}(1)} = \frac{k [\text{NO}]_{(3)}^x [\text{H}_2]_{(3)}^y}{k [\text{NO}]_{(1)}^x [\text{H}_2]_{(1)}^y}$$

$$\frac{0.0120\text{M}/\text{min}}{0.00600\text{M}/\text{min}} = 2 = \frac{k \cancel{[0.0100]}^x [0.0200]^y}{k \cancel{[0.0100]}^x [0.0100]^y} = \frac{[0.0200]^y}{[0.0100]^y}$$

$$\frac{[0.0200]^y}{[0.0100]^y} = \left[\frac{0.0200}{0.0100} \right]^y$$

$$\log \left(\left[\frac{0.0200}{0.0100} \right]^y = 2 \right)$$

$$\log \left(\frac{0.0200}{0.0100} \right)^y = \log 2$$

$$y \log(2) = \log 2$$

$$y = 1$$

Now that “y” is known, we may solve for x in a similar manner:

$$\frac{\text{Rate}(1)}{\text{Rate}(2)} = \frac{k [\text{NO}]_{(1)}^x [\text{H}_2]_{(1)}^y}{k [\text{NO}]_{(2)}^x [\text{H}_2]_{(2)}^y}$$

$$\frac{0.00600}{0.144} = \frac{k [0.0100]^x [0.0100]}{k [0.0200]^x [0.0300]}$$

$$\frac{1}{24} = \left(\frac{1}{2} \right)^x \times \left(\frac{1}{3} \right)$$

$$\left(\frac{1}{2} \right)^x = \frac{1}{8}$$

$$x \log \left(\frac{1}{2} \right) = \log \left(\frac{1}{8} \right)$$

$$x = 3$$

The Rate Law is:

$$\text{Rate}(\text{M}/\text{min}) = k [\text{NO}]^3 [\text{H}_2]$$

To find the rate constant, choose one set of data and solve:

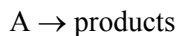
$$0.0120 \frac{\text{M}}{\text{min}} = k (0.0100\text{M})^3 (0.0200\text{M})$$

$$k = \frac{0.0120 \frac{\text{M}}{\text{min}}}{(0.0100\text{M})^3 (0.0200\text{M})} = \frac{0.0120 \frac{\text{M}}{\text{min}}}{(0.0100)^3 (0.0200)\text{M}^4}$$

$$k = 6.00 \times 10^5 \frac{\text{M}^{-3}}{\text{min}}$$

Integrated Rate Laws: time dependence of concentration

For a first order process, the rate law can be written:



$$\text{Rate}(\text{Ms}^{-1}) = -\frac{\Delta[A]}{\Delta t} = k[A]$$

This is the “*average rate*”

If one considers the infinitesimal changes in concentration and time the rate law equation becomes:

$$\text{Rate}(\text{Ms}^{-1}) = -\frac{d[A]}{dt} = k[A]$$

This is the “*instantaneous rate*”

Integrating in terms of d[A] and dt:

$$\int_{[A]_0}^{[A]} \frac{d[A]}{[A]} = -k \int_0^t dt$$

where $[A] = [A]_0$ at time $t = 0$
and $[A] = [A]$ at time $t = t$

$$\int_{[A]_0}^{[A]} \frac{d[A]}{[A]} = -k \int_0^t dt \quad \longrightarrow \quad \ln\left(\frac{[A]}{[A]_0}\right) = -kt$$

Taking the exponent to each side of the equation:

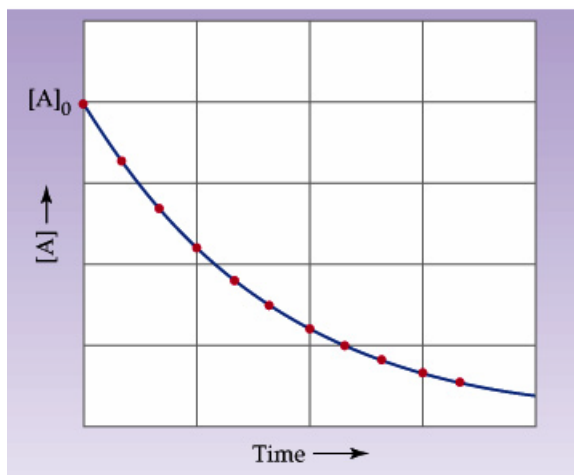
$$\frac{[A]}{[A]_0} = e^{-kt} \quad \text{or} \quad [A] = [A]_0 e^{-kt}$$

Conclusion: The concentration of a reactant governed by first order kinetics falls off from an initial concentration exponentially with time.

Recognizing a first order process: $A \rightarrow \text{products}$

Whenever the conc. of a reactant falls off exponentially, the kinetics follow first order.

$$[A] = [A]_0 e^{-kt}$$

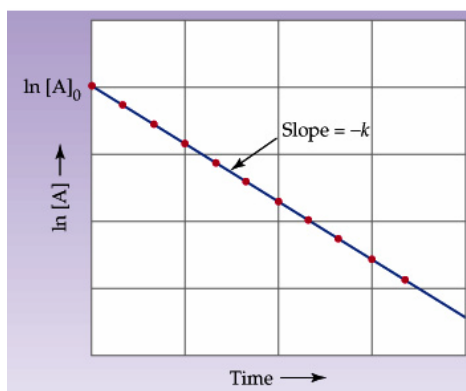


Determining the Rate constant for a first order process

Taking the log of the integrated rate law for a first order process we find:

$$\ln([A] = [A]_0 e^{-kt}) \longrightarrow \ln[A] = \ln[A]_0 - k \times t$$

A plot of $\ln[A]$ versus time (t) is a straight line with slope $-k$ and intercept $\ln[A]_0$



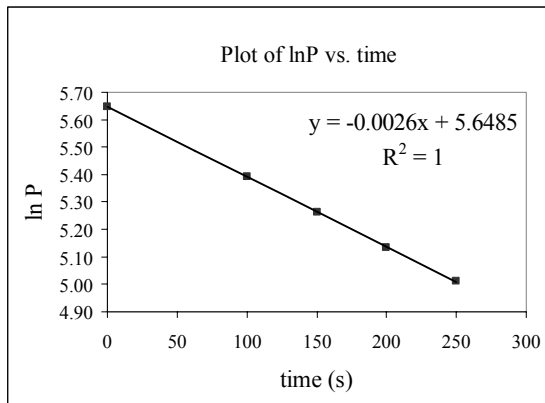
Example: The rate of decomposition of azomethane ($C_2H_6N_2$) was studied by monitoring the partial pressure of the reactant as a function of time.

Determine if the data below support a first order reaction.

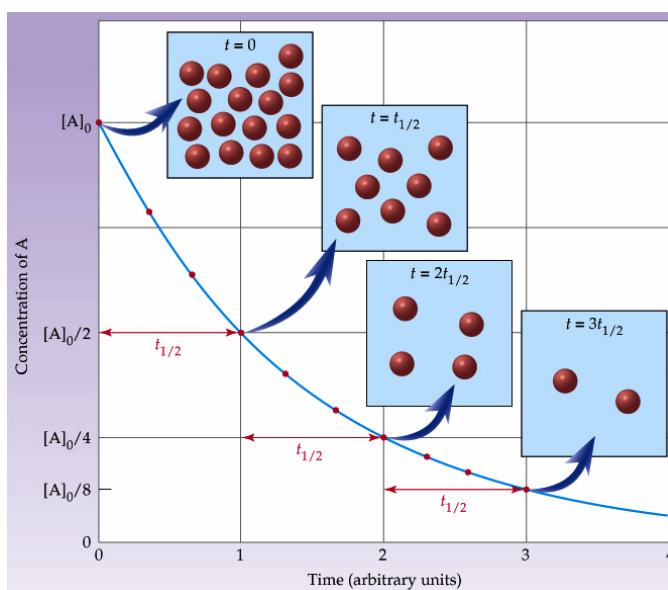
Calculate the rate constant for the reaction.

Time (s)	P (mmHg)	ln (P)
0	284	5.65
100	220	5.39
150	193	5.26
200	170	5.14
250	150	5.01

$$k = 2.6 \times 10^{-3} s^{-1}$$



Reaction Half-Life



Reaction Half-life:

Half-life is the time taken for the concentration of a reactant to drop to half its original value.

$$[A] = \frac{[A]_0}{2}$$

For a first order process the half life ($t_{1/2}$) is found mathematically from:

$$(1) \ln[A] = -kt + \ln[A]_0$$

$$(2) \ln[A] - \ln[A]_0 = -kt$$

$$(3) \ln\left(\frac{[A]}{[A]_0}\right) = -kt$$

$$(4) \ln\left(\frac{[A]_0}{[A]}\right) = kt$$

$$(5) \ln\left(\frac{[A]_0}{[A]_0/2}\right) = kt_{1/2}$$

$$t_{1/2} = \frac{\ln 2}{k} = \frac{0.693}{k}$$

A certain reaction proceeds through first order kinetics.

The half-life of the reaction is 180 s.

What percent of the initial concentration remains after 900s?

Step 1: Determine the magnitude of the rate constant, k.

$$t_{1/2} = \frac{\ln 2}{k} = \frac{0.693}{k} \quad k = \frac{\ln 2}{t_{1/2}} = \frac{\ln 2}{180\text{s}} = 0.00385\text{s}^{-1}$$

Using the integrated rate law, substituting in the value of k and 900s we find:

$$\frac{[A]}{[A]_0} = e^{-kt} \longrightarrow \frac{[A]}{[A]_0} = e^{-0.00385\text{s}^{-1} \times 900\text{s}} = 0.0312$$

Since the ratio of [A] to $[A]_0$ represents the fraction of $[A]_0$ that remains, the % is given by:

$$100 \times 0.0312 = 3.12\%$$

For a Second Order Process:



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

$$\text{Rate}(\text{Ms}^{-1}) = -\frac{d[A]}{dt} = k[A]^2$$

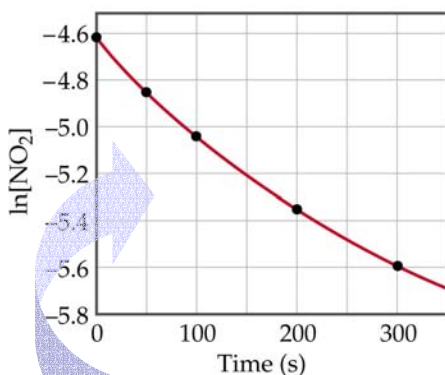
Integrating as before we find:

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

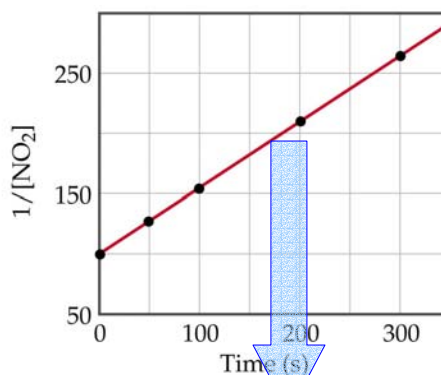
A plot of $1/[A]$ versus t is a straight line with slope k and intercept $1/[A]_0$

For a second order reaction, a plot of $\ln[A]$ vs. t is **not linear**.

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



Non-linearity indicates that the reaction is not first order.



Slope = k (rate constant)

Half-life for a second-order reaction

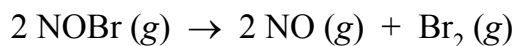
Unlike a first order reaction, the rate constant for a second order process depends on and the initial concentration of a reactant.

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

at the half-life, $[A]_t = \frac{1}{2} \times [A]_0$

Substituting and solving, $t_{1/2} = \frac{1}{k[A]_0}$

EXAMPLE: The reaction



is a second order reaction with respect to NOBr.

$k = 0.810 \text{ M}^{-1}\cdot\text{s}^{-1}$ at 10°C .

If $[\text{NOBr}]_0 = 7.5 \times 10^{-3} \text{ M}$, how much NOBr will be left after a reaction time of 10 minutes?

Determine the half-life of this reaction.

SOLUTION: One can solve for the amount of NOBr after 10 minutes by substituting the given data into the integrated rate law for a second-order reaction.

$$\frac{1}{[\text{NOBr}]_t} = kt + \frac{1}{[\text{NOBr}]_0} \quad (\text{Second Order})$$

$$\frac{1}{[\text{NOBr}]_t} = (0.810 \text{ M}^{-1} \cdot \text{s}^{-1}) \times (600 \text{ s}) + \frac{1}{7.5 \times 10^{-3} \text{ M}}$$

$$\frac{1}{[\text{NOBr}]_t} = 6.19 \times 10^2 \text{ M}^{-1}$$

$$[\text{NOBr}]_t = 1.6 \times 10^{-3} \text{ M}$$

To determine the half-life for this reaction, we substitute the initial concentration of NOBr and the rate constant for the reaction into the equation for the half-life of a second-order reaction.

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

$$t_{1/2} = \frac{1}{0.810 \text{ M}^{-1} \cdot \text{s}^{-1} (7.5 \times 10^{-3} \text{ M})} = 160 \text{ s}$$

The Arrhenius Equation:

Temperature dependence of the Rate Constant

Most reactions speed up as temperature increases.

(*example:* food spoils when not refrigerated.)

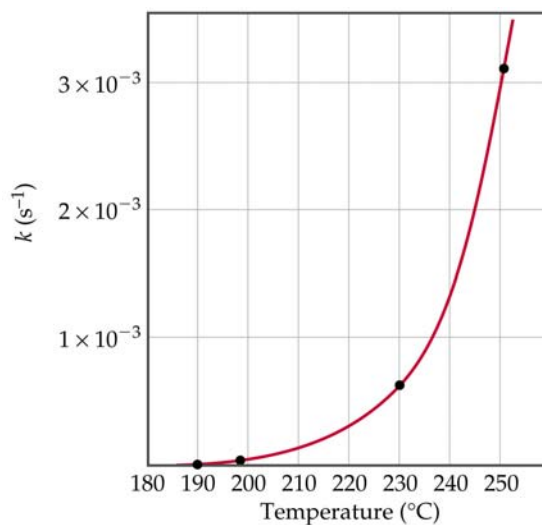
$$k = f(T)$$

Where “f” is some function.

The magnitude of a first order rate constant is seen to increase exponentially with an increase in temperature.

Therefore one can conclude that:

$$k(T) \propto e^{f(T)}$$



Why would k (along with the rate) increase with temperature?
Let's go back to *Kinetic Molecular Theory* to understand...

The Collision Model: In order for molecules to react they must collide.

As temperature increases, the molecules move faster and the collision frequency increases.

Therefore, the greater the number of collisions the faster the rate.

Thus reaction **rate** should **increase** with an increase in temperature.

Also, the more molecules present, the greater the probability of collision and the faster the rate.

Thus reaction **rate** should **increase** with an increase in the concentration of reactant molecules.

Activation Energy

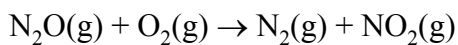
Arrhenius: Molecules must possess a minimum amount of energy to react. Why?

- (1) In order to form products, bonds must be broken in the reactants.
- (2) Bond breakage requires energy.
- (3) Molecules moving too slowly, with too little kinetic energy, don't react when they collide.

The Activation energy, E_a , is the minimum energy required to initiate a chemical reaction.

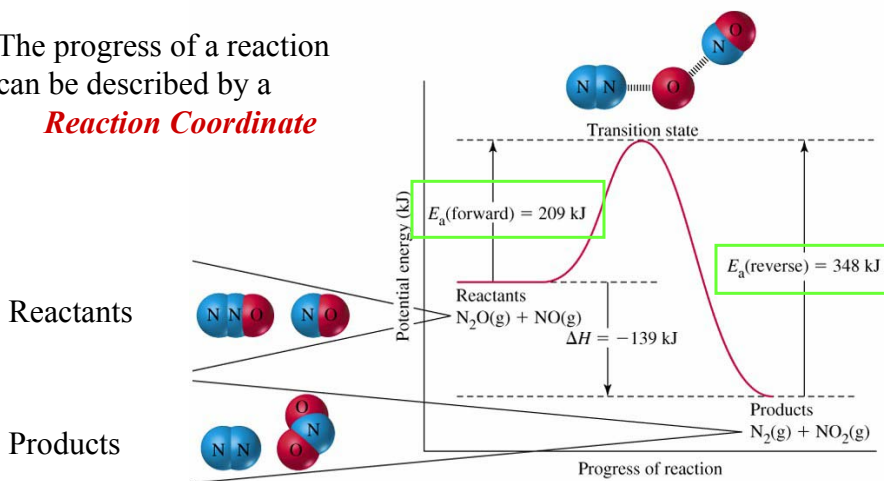
E_a is specific to a particular reaction.

Consider the reaction:

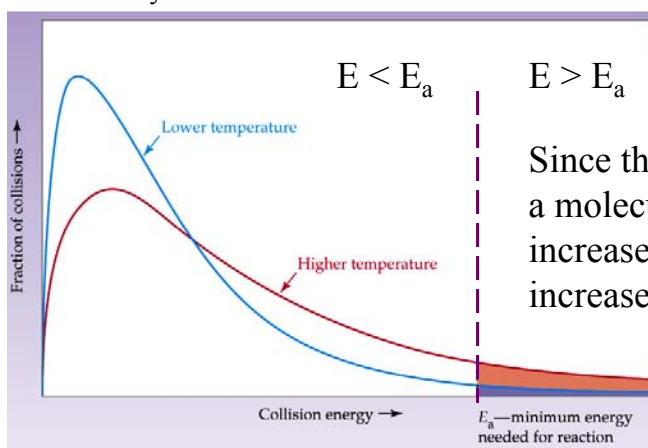


The progress of a reaction can be described by a

Reaction Coordinate



Recall for KMT that the temperature for a system of particles is described by a distribution.

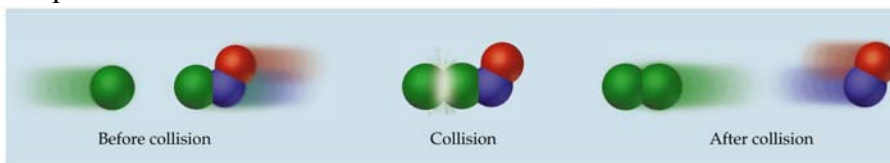


Since the probability of a molecule reacting increases, the rate increases.

At higher temps, more particles have enough energy to go over the barrier.

Orientation factors into the equation

The orientation of a molecule during collision can have a profound effect on whether or not a reaction occurs.



(a) Effective collision



(b) Ineffective collision

Some collisions do not lead to reaction even if there is sufficient energy.

The Arrhenius Equation

Arrhenius discovered that most reaction-rate data obeyed an equation based on three factors:

- (1) The number of collisions per unit time.
- (2) The fraction of collisions that occur with the correct orientation.
- (3) The fraction of the colliding molecules that have an energy greater than or equal to E_a .

From these observations Arrhenius developed the aptly named *Arrhenius equation*.

Arrhenius equation

$$k = Ae^{\frac{-E_a}{RT}}$$

k is the rate constant

T is the temperature in K

E_a is the activation energy

R is the ideal-gas constant (8.314 J/Kmol)

A is known the *frequency or pre-exponential factor*

In addition to carrying the units of the rate constant, “ A ” relates to the frequency of collisions and the orientation of a favorable collision probability

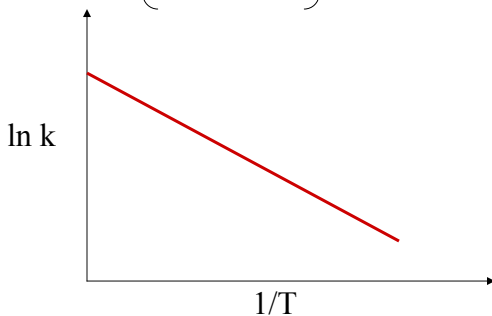
Both A and E_a are *specific to a given reaction*.

Determining the Activation Energy

E_a may be determined experimentally.

First take natural log of both sides of the Arrhenius equation:

$$\ln \left(k = Ae^{\frac{-E_a}{RT}} \right) \longrightarrow \ln k = -\frac{E_a}{RT} + \ln A$$



Golly-gee, what do we have once again...

A plot of $\ln k$ vs $1/T$ will have a slope of $-E_a/R$ and a y-intercept of $\ln A$.

Determining the Activation Energy

One can determine the activation energy of a reaction by measuring the rate constant at two temperatures:

Writing the Arrhenius equation for each temperature:

$$\ln k_1 = -\frac{E_a}{RT_1} + \ln A \quad \ln k_2 = -\frac{E_a}{RT_2} + \ln A$$

If one takes the natural log of the ratio of k_2 over k_1 we find that:

$$\ln\left(\frac{k_2}{k_1}\right) = \ln k_2 - \ln k_1$$

Substituting in the values for E_a into the equation:

$$\ln k_2 - \ln k_1 = \left(-\frac{E_a}{RT_2} + \ln A\right) - \left(-\frac{E_a}{RT_1} + \ln A\right)$$

Lookie what happens...



Knowing the rate at two temps yields the rate constant.

or

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

Knowing the E_a and the rate constant at one temp allows one to find $k(T_2)$

Example: The activation energy of a first order reaction is 50.2 kJ/mol at 25°C. At what temperature will the rate constant double?

$$(1) \quad k_2 = 2k_1 \qquad (2) \quad \ln\left(\frac{k_2}{k_1}\right) = \ln\left(\frac{2k_1}{k_1}\right) = \ln(2) = \frac{E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

$$(3) \quad \frac{E_a}{R} = \frac{50.2 \text{ kJ/mol} \times \frac{10^3 \text{ J}}{1 \text{ kJ}}}{8.314 \frac{\text{J}}{\text{mol} \cdot \text{K}}} = 6.04 \times 10^3 \text{ K}$$

$$(4) \quad \ln(2) = 0.693 = 6.04 \times 10^3 \text{ K} \times \left(\frac{1}{298 \text{ K}} - \frac{1}{T_2} \right)$$

A 10°C change of temperature doubles the rate!!

$$(5) \quad \frac{1}{T_2} = 3.24 \times 10^{-3} \text{ K}^{-1} \longrightarrow \boxed{T_2 = 308 \text{ K}}$$