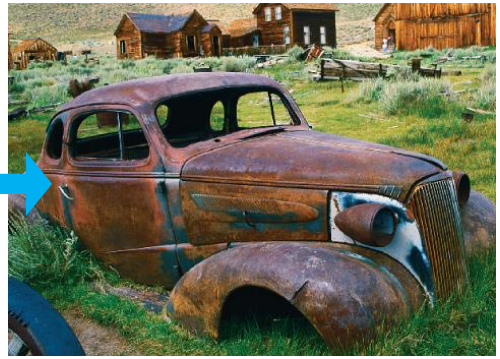
CHEMICAL KINETICS

Thermodynamics verses Kinetics

Thermodynamics tells us ***which way*** a chemical reaction will go.

Kinetics tells us ***how fast*** a chemical reaction will go as well has ***how to control*** the rate.

Fast



Slow

Reaction Rates

Chemical rates are **changes in concentration** over a **time interval**.

Rates can be either an (1) **average** or (2) **instantaneous**.

The advantage of an (1) **average** rate is they are *easy to calculate*. The disadvantage is they tend to be very general, and *not exact*.

The advantage of an (2) **instantaneous** rate is it give very specific, giving *exact information*. The disadvantage is the time it takes to *setup and make the calculation.*

Average Reaction Rates

Average rates change in molar concentration of **reactants**, **R**

$\Delta[R] = [R]_{t2} - [R]_{t1}$ divided by the time interval $\Delta t = t_2 - t_1$:

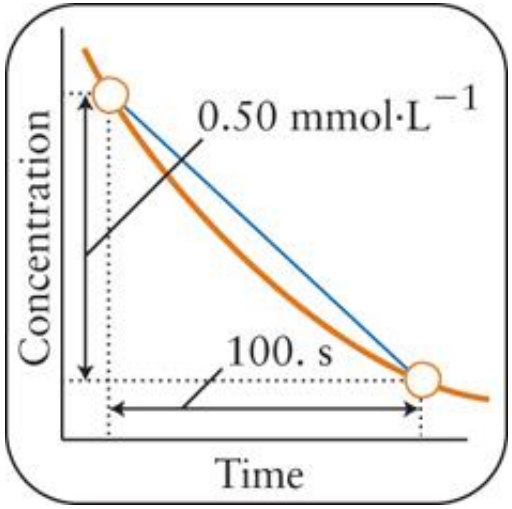
Average rate of ***consumption*** of **R** $= -\frac{\Delta[R]}{\Delta t}$

Note on the "-" meaning reactants disappear.

For **products P** $= \frac{\Delta[P]}{\Delta t}$

Remember that [ ] stands for concentration or $mol \cdot L^{-1}$

Example 1: Suppose we are studying the reaction $2\ HI(g) \rightarrow H_2(g) + I_2(g)$ and find that, in an interval of 100. s, the concentration of HI decreases from 4.00 mmol·L^{-1} to 3.50 mmol·L^{-1}. What is the average reaction rate ?



Since we are watching reactants go away, we expect to see a negative slope.

$$\mathbf{R} = -\frac{\Delta[R]}{\Delta t} = -\frac{[R]_{t2} - [R]_{t1}}{t_2 - t_1} = -\frac{(3.50 - 4.00)\ \text{mmol·L}^{-1}}{100.\ \text{s}}$$

$$= 5.0 \times 10^{-3}\ \text{mmol HI·L}^{-1}\text{·s}^{-1}$$

We just calculated the blue line.

Note: 10^{-3} mmol = μmol, so in this example -5.0×10^{-3} mmol HI·L^{-1}·s^{-1} = -5.0 μmol HI·L^{-1}·s^{-1}

Average Reaction Rates based on Stoichiometry

To avoid confusion when reporting rates of a reaction, rates are always reported as *stoichiometric coefficients* relationships. This way the rate is the same for that reaction, no matter which species the rate is reported for. For example,

$2\ HI(g) \rightarrow\ H_2(g) + I_2(g)$

$$R = -\frac{1}{2}\frac{\Delta[HI]}{\Delta t} = \frac{\Delta[H_2]}{\Delta t} = \frac{\Delta[I_2]}{\Delta t}$$

(a) What is the average rate of formation of H_2 in the same reaction?

$R = \frac{1}{2}(5.0 \times 10^{-3}\ \text{mmol HI}\cdot L^{-1}\cdot s^{-1}) = 2.5 \times 10^{-3}\ \text{mmol } H_2\cdot L^{-1}\cdot s^{-1}$

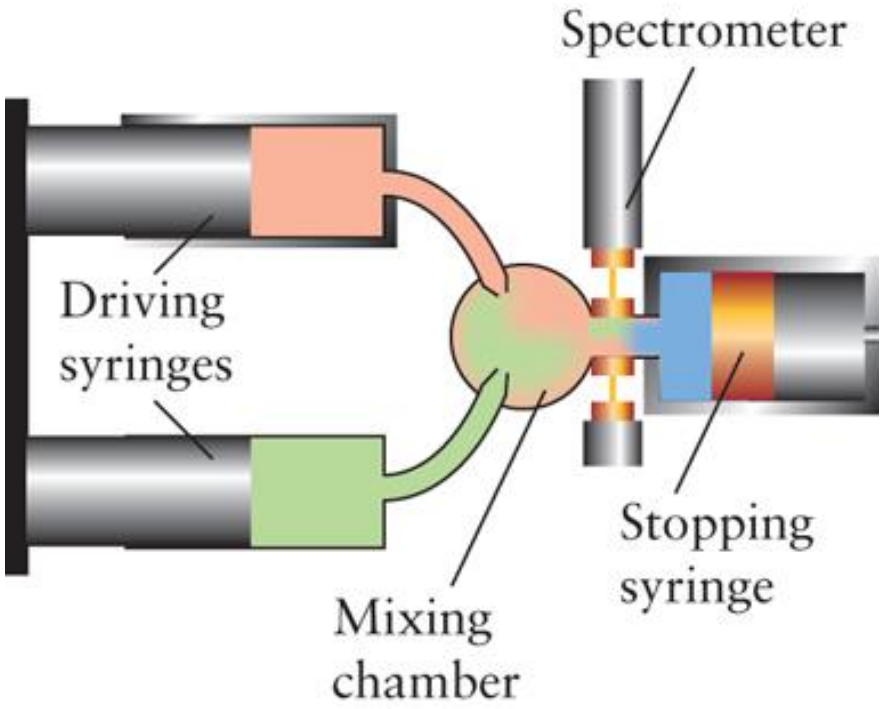
(b) What is the unique average rate, both over the same period?

$R = -\frac{1}{2}\frac{\Delta[HI]}{\Delta t} = \frac{\Delta[H_2]}{\Delta t} = \frac{\Delta[I_2]}{\Delta t} = \frac{1}{2}(5.0 \times 10^{-3}\ \text{mmol HI}\cdot L^{-1}\cdot s^{-1}) =$
$2.5 \times 10^{-3}\ \text{mmol } H_2\cdot L^{-1}\cdot s^{-1}$

Monitoring rates of chemical reactions

In a **stopped-flow experiment**, the driving syringes on the left push reactant solutions into the mixing chamber, and the stopping syringe on the right stops the flow.

The progress of the reaction is then monitored spectroscopically as a function of time.

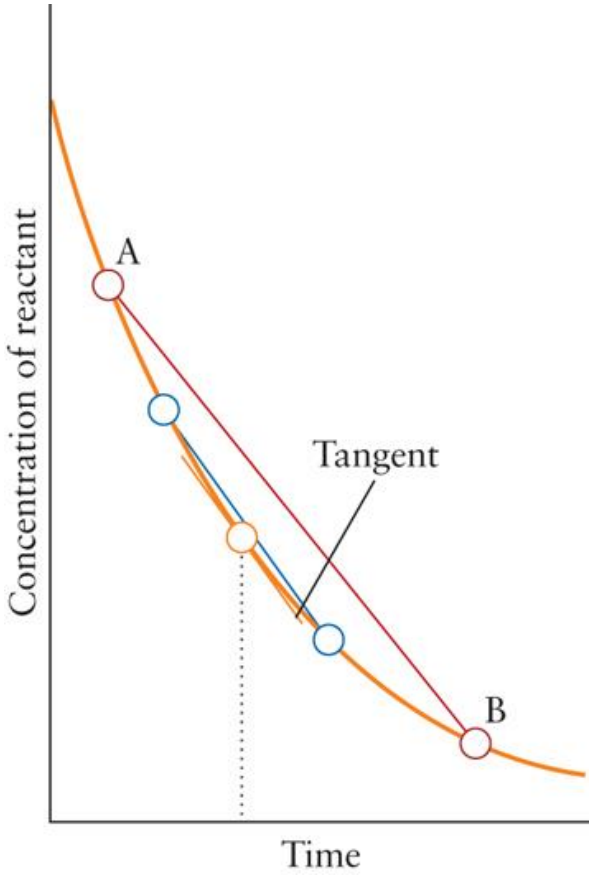


Instantaneous Rate of Reaction

Reactions slow down as reactants are used up.

An “instant” rate is found by measuring two concentration, *as close together in time* as possible.

A better method is to find the **slope of the tangent** that provides the ***instantaneous rate***.



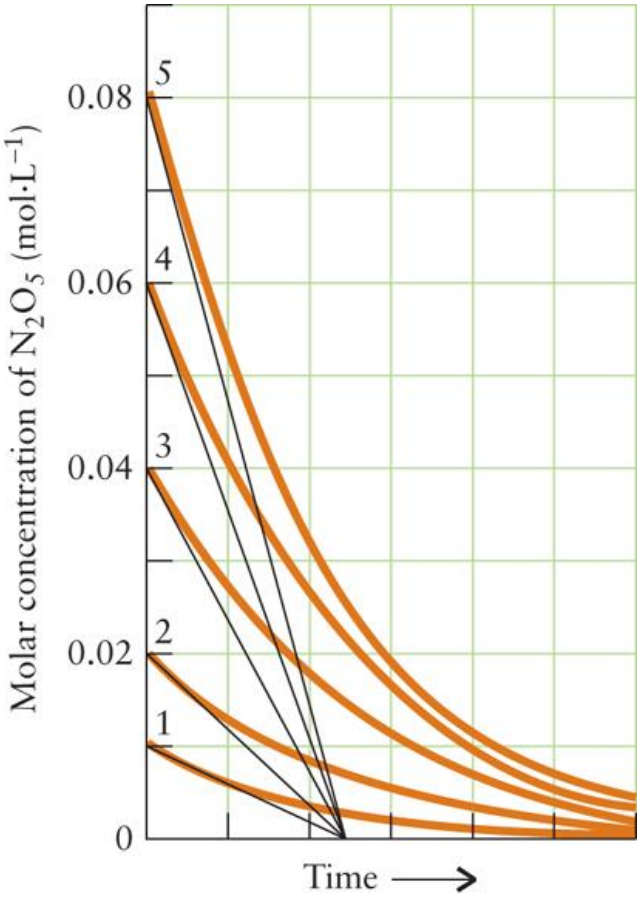
Though a computer can calculate tangent lines, we need to devise methods to **determine the equations for these lines**, which are called **rate laws**.

The Order of a Rate Law

There are two parts to every rate law. (1) how fast the line changes, or speed (initial rate) and (2) the shape of the line, called the rate law.

We will start by showing a typical experiment to find part 1, speed.

To avoid complications, arising from products interfering with our measurements, observations are made in just the first few seconds of the beginning of the reaction.



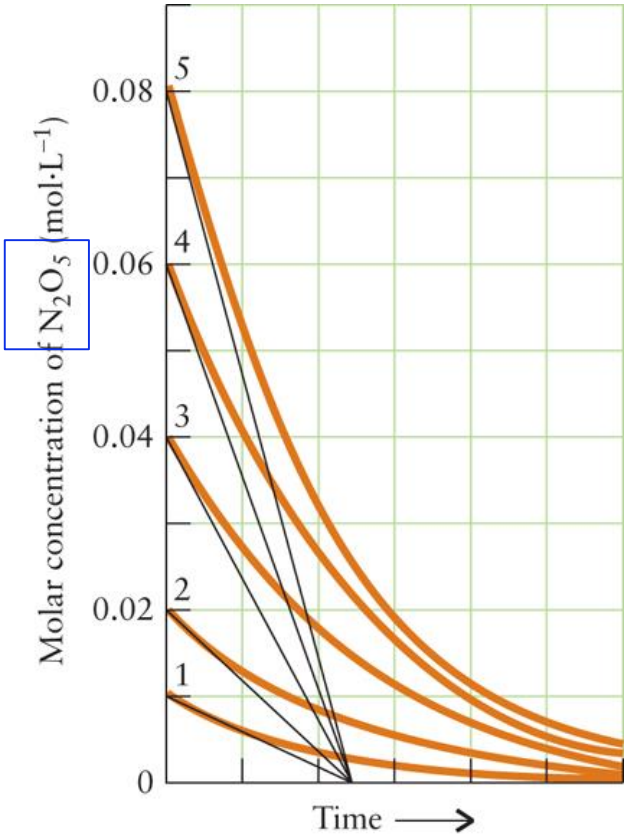
The Order of a Rate Law

For instance making five seperate reactions with different concentrations:

$2\ N_2O_5(g) \rightarrow 4\ NO_2\ (g) + O_2\ (g)$

In each flask (reaction), after a few seconds we look to see how much of the **reactants** has discengrated.

Next we plot $\dfrac{\text{initial rate}}{\text{concentration}}$



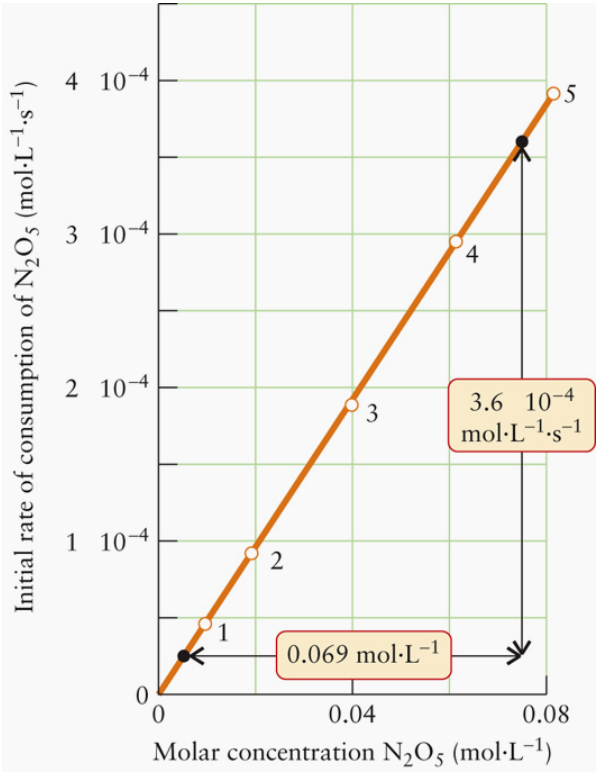
The Order of a Rate Law

Plotting $\frac{\text{initial rate}}{\text{concentration}}$ we get a straight line.

The slope of the line, k , is the speed (rate of change), here $5.2 \times 10^{-3}\ s^{-1}$.

$\frac{\text{initial rate}}{[N_2O_5]} = k$ (slope)

rate = $k[N_2O_5]$ is called a rate law.



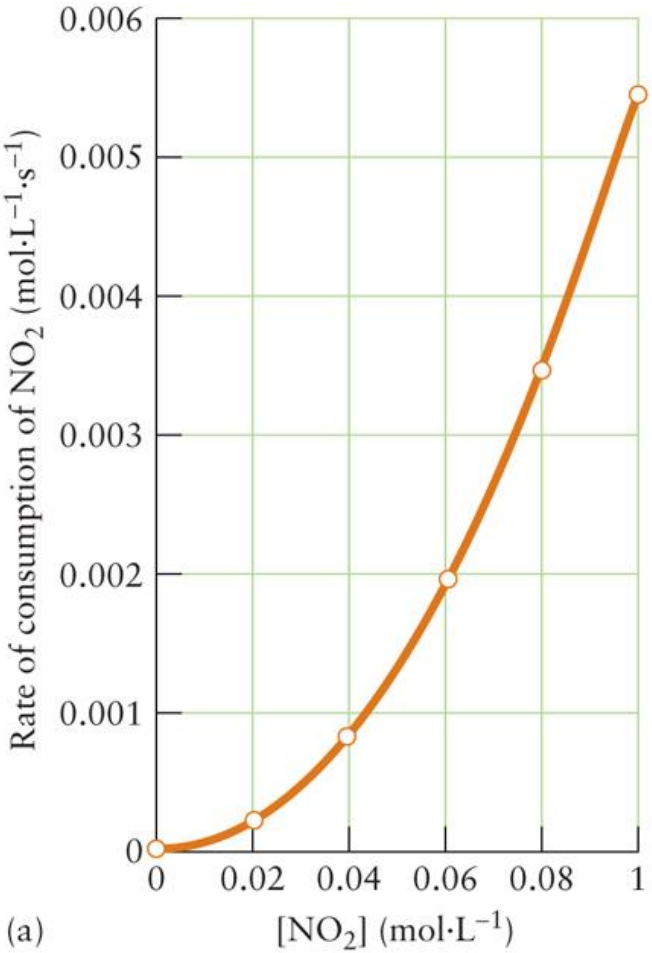
The Order of a Rate Law

Here a different reaction: $2NO_2(g) \rightarrow 2NO(g) + O_2(g)$.

Plotting $\frac{\text{initial rate}}{[N_2O_5]}$

However, in our five flasks of varing-concentration-experiment, we do not get a straight line.

We need to re-plot our data differently.

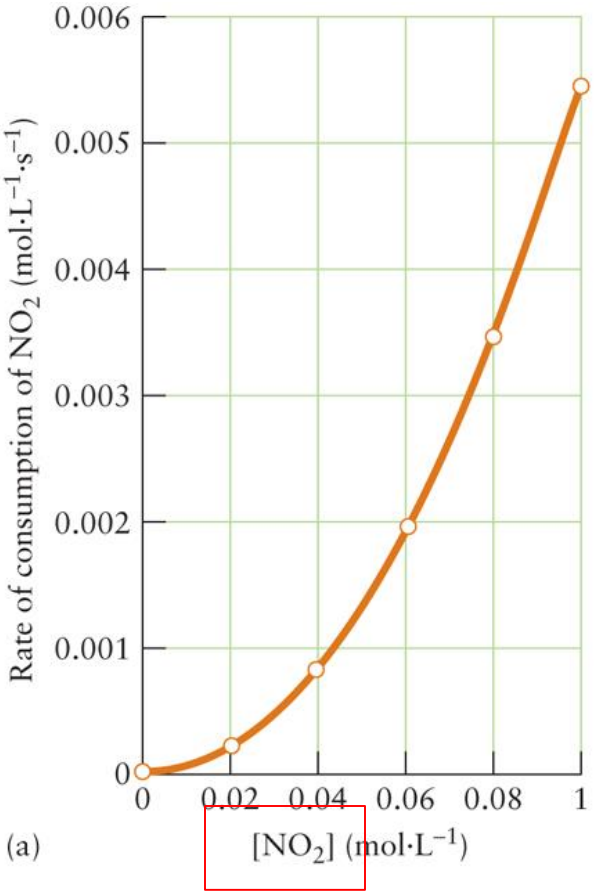


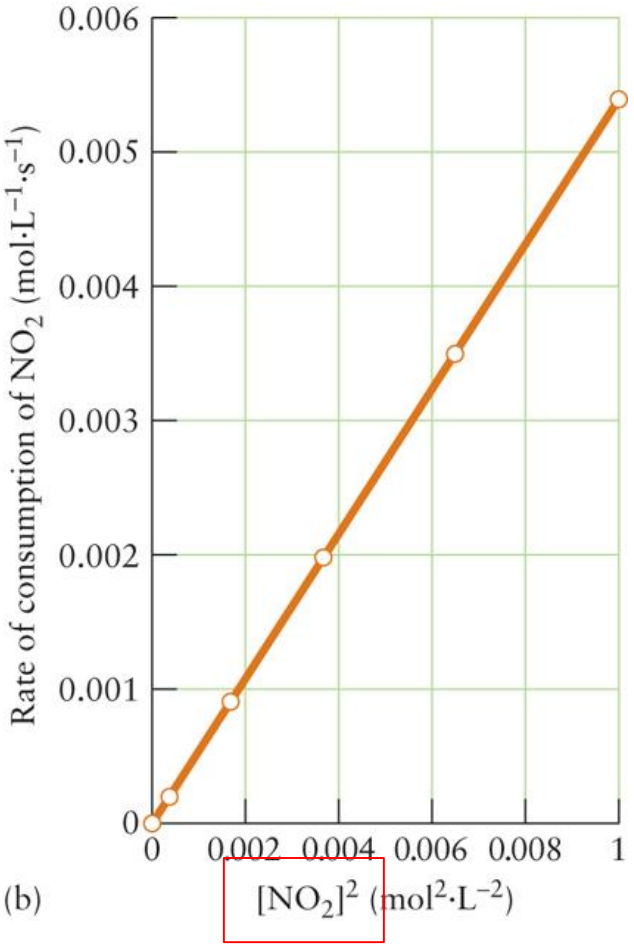
The Order of a Rate Law

We re-plot $\frac{\text{initial rate}}{[NO_2]^2}$ = k, and we do get straight line.

The rate law is now

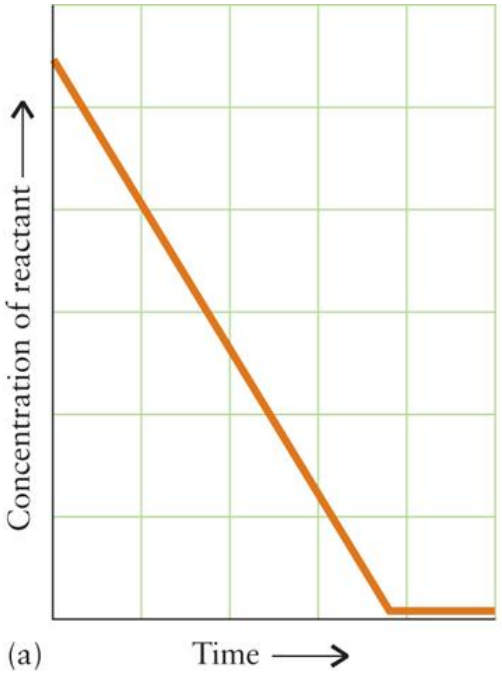
rate = $k[NO_2]^2$



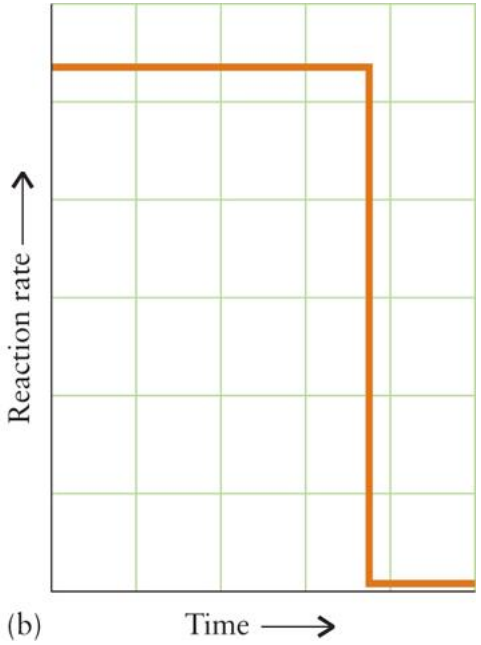


The Order of a Rate Law

Here a different reaction: $2NH_3\,(g) \rightarrow N_2(g) + 3H_2(g)$



The concentration falls at a constant rate until reactants are exhausted.



Once exhausted the rate falls abruptly to zero.

$$\frac{\text{initial rate}}{\text{concentration}} = \frac{\text{initial rate}}{1} = k$$

rate = k

The Order of a Rate Law

Rate = rate constant × [concentration]^{a} where **a** is called the **order**

rate = k	zero order
rate = k[N_2O_5]	first order
rate = k[NO_2]^2	second order

Orders gives us important insight as to how the reaction works. The overall order is 2 for a second order, and 1 or 0 for first and zero order.

Most reactions are either first or second order.

In zero order cases, only a catalyts can control the rate.

The Order of a Rate Law

In general, if Rate = $k [A]^a[B]^b$ then the overall order is the sum of the powers a + b + ...

Reaction	Rate law	Temp (K)	Rate constant
$2N_2O \rightarrow 2N_2 + O_2$	$K[N_2O]$	1000	$0.76\ s^{-1}$
$H_2 + I_2 \rightarrow 2\ HI$	$K[H_2][I_2]$	500	4.3×10^{-7} $L \cdot mol^{-1} \cdot s^{-1}$
		600	4.4×10^{-4}
		700	6.3×10^{-2}
$H_3O^+ + OH^- \rightarrow 2\ H_2O$	$K[H_3O^+][OH^-]$	298	1.5×10^{11} $L \cdot mol^{-1} \cdot s^{-1}$

Example 2: When the NO concentration is doubled, the rate of the reaction $2\ NO(g) + O_2(g) \rightarrow 2\ NO_2(g)$ increases by a factor of 4. When both the O_2 and the NO concentrations are doubled, the rate increases by a factor of 8. What are (a) the reactant orders, (b) the overall order of the reaction, and (c) the units of k if the rate is expressed in moles per liter per second ?

(a) To find the order of a reaction we need to find the powers in our rate expression, for a generic expression we know

$Rate = k\,[A]^a[B]^b$

We know that by doubling the [NO] and holding the $[O_2]$ constant, the rate increased by 4, or $\underbrace{4 = 2^a}_{rate = [A]^a}$, so a = 2 to make this true.

In a second experiment doubling both the [NO] and $[O_2]$ the rate goes up 8 times faster, which means $8_{rate} = 2^a \times 2^b$, since we know a = 2, then $8 = 4 \times 2^b$, therefore b = 1, so that $8 = 4 \times 2^1$.

Example 2: When the NO concentration is doubled, the rate of the reaction $2\ NO(g) + O_2(g) \rightarrow 2\ NO_2(g)$ increases by a factor of 4. When both the O_2 and the NO concentrations are doubled, the rate increases by a factor of 8. What are (a) the reactant orders, (b) the overall order of the reaction, and (c) the units of k if the rate is expressed in moles per liter per second ?

(b) Overall order for Rate = $k\ [A]^a[B]^b$ is a + b, so here, a = 2, b = 1, or 2 + 1 = 3 or third order.

(c) We know that we must **keep the rate as Ms^{-1}**, so the units of k must change to make that so. So far we have rate = $k\ [NO]^2[O_2]^1$, units on the right are $k(M)^2(M)$ so to keep the units on both sides of the equation the same k must be $M^{-2}s^{-1}$ or $mol^{-2}L^2s^{-1}$ or $\frac{L^2}{mol^2 s}$.

Negative Orders

Orders can be negative, (concentration)$^{-1}$, $[A]^{-1} = \frac{1}{[A]}$.

This species *slows down* and *reverses* the reaction!

Decomposition of ozone is such an example.

$2O_3(g) \rightarrow 3O_2(g)$

The experimentally determined rate law is

$$\text{Rate} = k\frac{[O_3]^2}{[O_2]} = k[O_3]^2[O_2]^{-1}$$

Determining orders and rate law from experimental data

From this data determine the (1) order, a & b, (2) rate constant, k, and (3) the rate expression.

$$\text{Rate} = k\,[A]^a[B]^b$$

Rates are measure experimentally.

	Initial Conc. ($mol \cdot L^{-1}$)			Initial rate
Exp.	BrO_3^-	Br^-	H_3O^+	mmole $BrO_3^- \cdot L^{-1} \cdot s^{-1}$
1	0.10	0.10	0.10	1.2
2	0.20	0.10	0.10	2.4
3	0.10	0.30	0.10	3.5
4	0.20	0.10	0.15	5.5

Example 3: find (1) order, a & b, (2) rate constant, k, and (3) the rate expression for the reaction

BrO_3^- (aq) + 5 Br^- (aq) + 6 H_3O^+ (aq) $\rightarrow$ 3 Br_2(aq) + 9 H_2O(l):

	Initial Conc. (mol·L^{-1})			**Initial rate**
Exp.	BrO_3^-	Br^-	H_3O^+	mmole BrO_3^- ·L^{-1}·s^{-1}
1	0.10	0.10	0.10	1.2
2	0.20	0.10	0.10	2.4
3	0.10	0.30	0.10	3.5
4	0.20	0.10	0.15	5.5

The plan is to find Rate = k $[BrO_3^-]^a[Br^-]^b[H_3O^+]^c$ here a, b, c, and k.

	Initial Conc. (mol·L^{-1})			Initial rate
Exp.	BrO_3^-	Br^-	H_3O^+	mmole BrO_3^- ·L^{-1}·s^{-1}
1	0.10	0.10	0.10	1.2
2	0.20	0.10	0.10	2.4
3	0.10	0.30	0.10	3.5
4	0.20	0.10	0.15	5.5

For instance if we double $[BrO_3^-]$ how much does rate go up?

Look at the difference between Experiment 1 and Experiment 2, the only thing changing is bromate, bromide and hydronium are held constant. The change in rate and concentrations are

$$\frac{\text{rate Exp 2}}{\text{rate Exp 1}} = \frac{2.4}{1.2} = 2 \text{ and } \frac{[BrO_3^-]^a \text{ Exp 2}}{[BrO_3^-]^a \text{Exp 1}} = \frac{.20^a}{.10^a} = 2$$

so (rate) $2 = 2^a$, so in this case we know a = 1.

	Initial Conc. (mol·L^{-1})			Initial rate
Exp.	BrO_3^-	Br^-	H_3O^+	mmole BrO_3^- ·L^{-1}·s^{-1}
1	0.10	0.10	0.10	1.2
2	0.20	0.10	0.10	2.4
3	0.10	0.30	0.10	3.5
4	0.20	0.10	0.15	5.5

Looking at Exp 1 and 3, bromide triples, and bromate and hydronium are the same, while the rate increases by 3.5/1.2 = 2.9, so $2.9 = 3^b$, so b is 1

Looking at Exp 2 and 4, hydronium increases 1.5, and bromate and bromide are the same, while the rate increases by 5.5/2.4 = 2.29, so $2.29 = 1.5^c$, so c is 2

Note: for "c" we could have used $2.29 = 1.5^c$ or $c = \frac{\ln 2.29}{\ln 1.5} = 2$

Our expression so far is Rate = k $[BrO_3^-]^1[Br^-]^1[H_3O^+]^2$.

The overall order is 1 + 1 + 2 = 4

To find k we return to the table and chose any experiment, plug the data in to find k.

Experiment	Initial concentration ($mol \cdot L^{-1}$)			Initial rate ($(mmol\ BrO_3^-) \cdot L^{-1} \cdot s^{-1}$)
	BrO_3^-	Br^-	H_3O^+	
1	0.10	0.10	0.10	1.2

We can use the data from experiment 1, for instance.

$1.2 \times 10^{-3}\ mol \cdot L^{-1}s^{-1} = k\ [0.10\ mol \cdot L^{-1}]^1[0.10\ mol \cdot L^{-1}]^1[0.10\ mol \cdot L^{-1}]^2$,

$$k = \frac{1.2 \times 10^{-3}\ mol \cdot L^{-1}s^{-1}}{[0.10\ mol \cdot L^{-1}]^1[0.10\ mol \cdot L^{-1}]^1[0.10\ mol \cdot L^{-1}]^2} = 12\ \frac{L^3}{mol^3 \cdot s} =$$

$12\ mol^{-3} \cdot L^3 \cdot s^{-1}$ which we can use for…

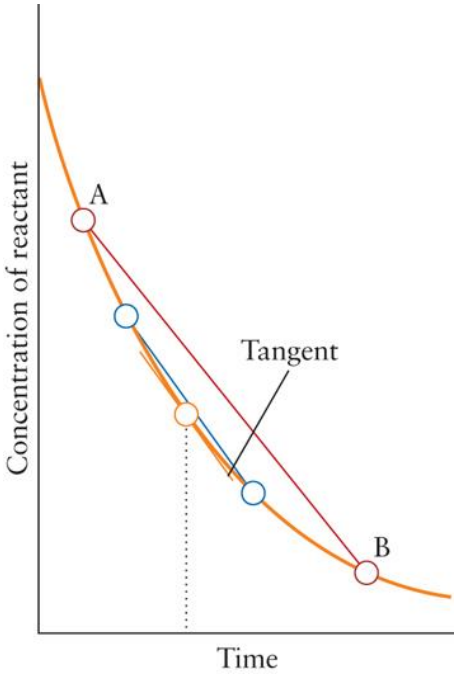
our final rate expression: Rate = $12\ mol^{-3} \cdot L^3 \cdot s^{-1}\ [BrO_3^-]^1[Br^-]^1[H_3O^+]^2$

Concentration & Time

Start by using our first order rate expression, Rate = k[A].

Our goal is to express the *Rate* as *[A] changes over time*.

Rate of disappearance of A: $-\frac{d[A]}{dt} = k[A]$ k: slope



rate = k	zero order
rate = k[A]	first order
rate = $k[A]^2$	second order

Concentration & Time

rate = k zero order

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

where the slope is –k (slope is decreasing or the speed is slowing down).

$[A]_0$: initial concentration of reactant

$[A]_t$: concentration of reactant at any time

rate = k[A] first order

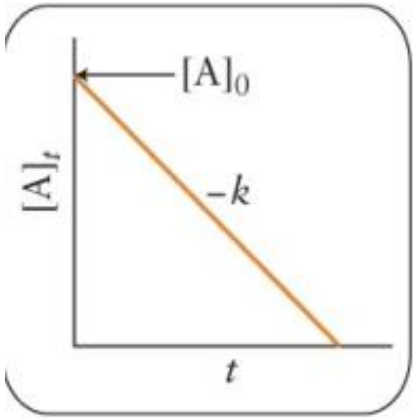
$$[A]_t = [A]_0 e^{-kt}$$

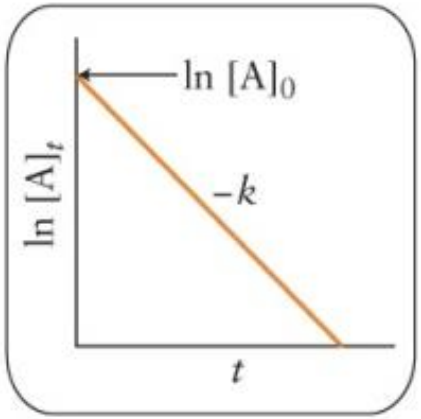
$$\ln [A]_t = \ln [A]_0 - kt$$

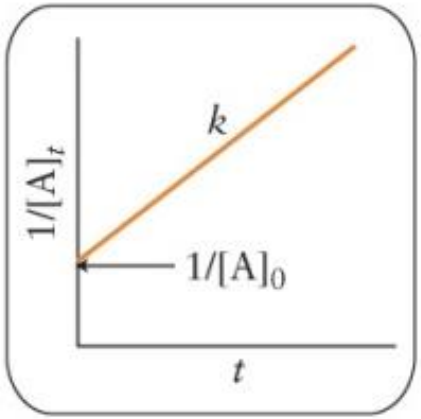
rate = $k[A]^2$ second order

$$\frac{1}{[A]_t} - \frac{1}{[A]_o} = kt$$

Order of reaction		
0	1	2
Rate = k	Rate = $k[A]$	Rate = $k[A]^2$
$[A]_t = -kt + [A]_0$	$[A]_t = [A]_0 e^{-kt}$	$[A]_t = \frac{[A]_0}{1 + [A]_0 t}$
		$\frac{1}{[A]_t} = \frac{1}{[A]_0} + kt$







$-k$	$-k$	k

k is positive.

K is “slope”.

“intercept” is about $[A_0]$.

Example 4: What concentration of N_2O_5 remains 10.0 min (600. s) after the start of its decomposition at 65°C when its initial concentration was 0.040 mol·L^{-1}? See Table 15.1 for the rate law.

$2\ N_2O_5(g) \rightarrow\ 4\ NO_2(g)\ + O_2(g)$, Rate of = $k[N_2O_5]$, where $k = 5.2\times10^{-3}\ s^{-1}$

Using $[A]_t = [A]_0 e^{-kt}$ we solve for $[N_2O_5]_t = [N_2O_5]_0 e^{-kt}$,

$[N_2O_5]_t = 0.040\ mol\cdot L^{-1} e^{-5.2 \times 10^{-3}\ s^{-1} \times 600.\ s} = 0.0018\ mol\cdot L^{-1}$

In 600. s, the conc. decreases 0.040 mol·L^{-1} to 0.0018 mol·L^{-1}.

Example 5: A sample of N_2O_5 is allowed to decompose by the following reaction: $2\ N_2O_5(g) \rightarrow 2NO_2(g) + O_2(g)$, Rate of = $k[N_2O_5]$, where $k = 5.2\times10^{-3}\ s^{-1}$. How long will it take for the concentration of N_2O_5 to decrease from 20. mmol·L^{-1} to 2.0 mmol·L^{-1} at 65°C?

$\ln [A]_t = \ln [A]_0 - kt$ we want to solve for t

$\text{Ln}(2.0\ \text{mmol}\cdot L^{-1}) = \ln(20.\ \text{mmol}\cdot L^{-1}) - 5.2\times10^{-3}\ s^{-1}\ t$,

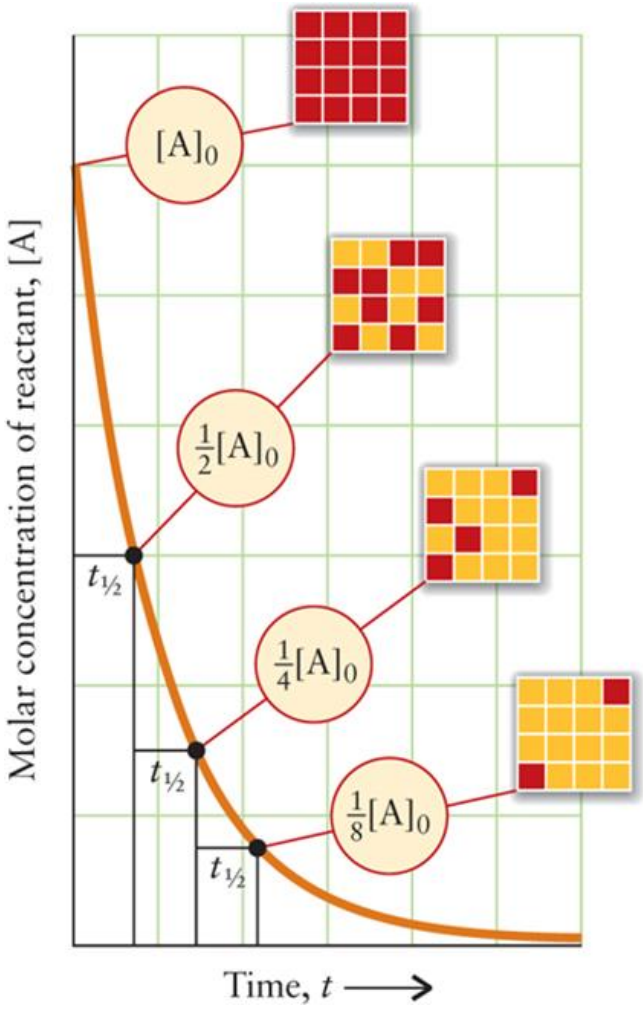
$0.69 = 3.0 - 5.2\times10^{-3}\ s^{-1}\ t$

$t = 440\ s$

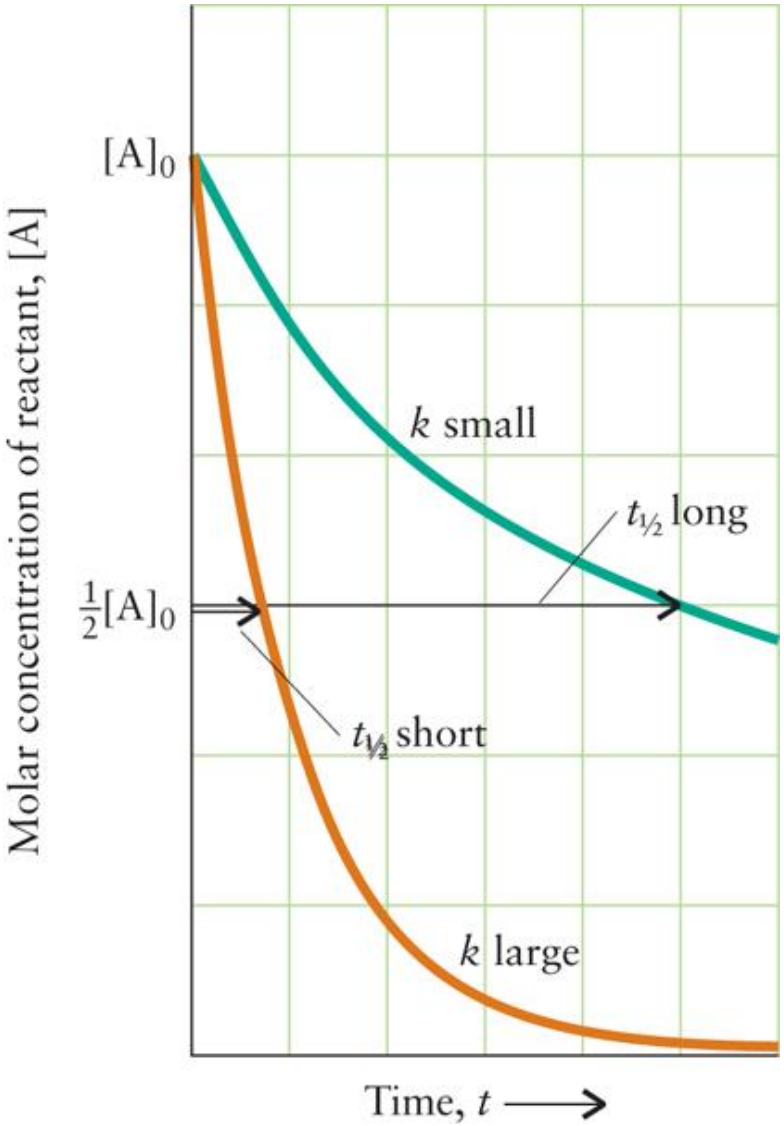
Half-Lives for First-Order Reactions

The half-life, $t_{1/2}$, is the time needed for its concentration to fall to one-half of its initial value.

There are many half-life processes, populations, chemical reactions, radioactive decay and others.



Half-Lives for First-Order Reactions



The **higher the value of k**, the *more rapid* the consumption of a reactant.

If the k is very large, for instance with **radioactive decay**, it would be considered hotter.

High values of k in a **population decay** means the population is dying quickly.

Finding $t_{1/2}$

Half-life is a first order process, $\ln \frac{[A]_t}{[A]_0} = -kt$ for t or $t_{½}$.

We arbitrarily pick $[A]_t = 1$, and $[A]_0 = 2$ that represents half of the material disappearing, starting at 2 and going to 1, this goes to

$$\ln \frac{1}{2} = -k\, t_{½}$$

Now rearrange the "-" and we get $\ln 2 = k\, t_{½}$

Solve for $t_{½}$, $t_{½} = \frac{\ln 2}{k}$

Half-life of a first-order

$$t_{½} = \frac{\ln 2}{k}$$

Example 6: Calculate (a) the number of half-lives and (b) the time required for the concentration of C_2H_6 to fall to one-sixteenth of its initial value as it dissociates into CH_3 radicals at 973 K.

$C_2H_6 \rightarrow 2\ CH_3$, $k[C_2H_6] = 5.5 \times 10^{-4}s^{-1}$

Part (a) needs two pieces of information, the total time and the half-life. We can get the half-life, by solved by using $t_{½} = \frac{\ln 2}{k}$ but part (b) is the total time.

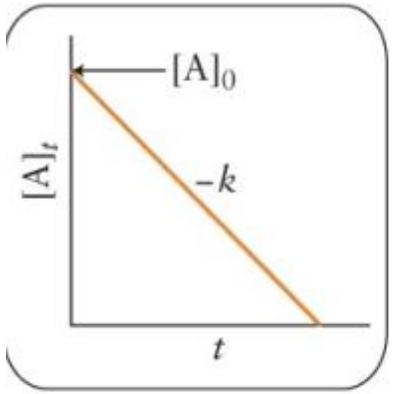
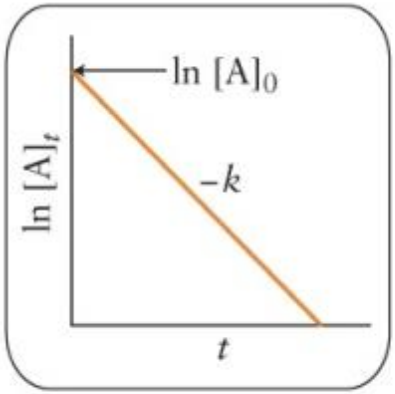
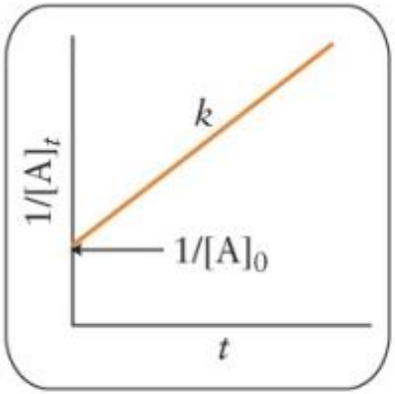
$t_{½} = \frac{\ln 2}{k}$, $\frac{\ln 2}{5.5 \times 10^{-4}s^{-1}} = 1300s$

Part (b) is to find the total time by solve for time, t,

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

$\text{Ln}(\frac{1}{16}) = \ln(1) - 5.5\times10^{-4}\ s^{-1}\ t \rightarrow\ t =\ 5000\ s$

Number of half-lives $\frac{\text{Total time}}{t_{½}} = \frac{5000\ s}{1300\ s}$ = 3.8 or 4 half-lives

Order of reaction		
0	1	2
Rate = k	Rate = $k[\mathrm{A}]$	Rate = $k[\mathrm{A}]^2$
$[\mathrm{A}]_t = -kt + [\mathrm{A}]_0$	$[\mathrm{A}]_t = [\mathrm{A}]_0 e^{-kt}$	$[\mathrm{A}]_t = \dfrac{[\mathrm{A}]_0}{1 + [\mathrm{A}]_0 t}$ $\dfrac{1}{[\mathrm{A}]_t} = \dfrac{1}{[\mathrm{A}]_0} + kt$
		
$-k$	$-k$	k
$t_{1/2} = \dfrac{[\mathrm{A}]_0}{2k}$ (not used)	$t_{1/2} = \dfrac{\ln 2}{k} \approx \dfrac{0.693}{k}$	$t_{1/2} = \dfrac{1}{k[\mathrm{A}]_0}$ (not used)

Reaction Mechanisms

Elementary reactions **describes a distinct event**, often a collision of particles.

Understanding how reactions takes place, requires us to propose a ***reaction mechanism***, a **sequence** of elementary reactions.

One Step: $O_3 + O_3 \rightarrow O_2 + O_2 + O_2$

Two Steps:
Step 1: $O_3 \rightarrow O_2 + O$ Intermediate reaction
Step 2: $O_3 + O \rightarrow O_2 + O_2$

The rate of a series reactions depends on the slowest step.

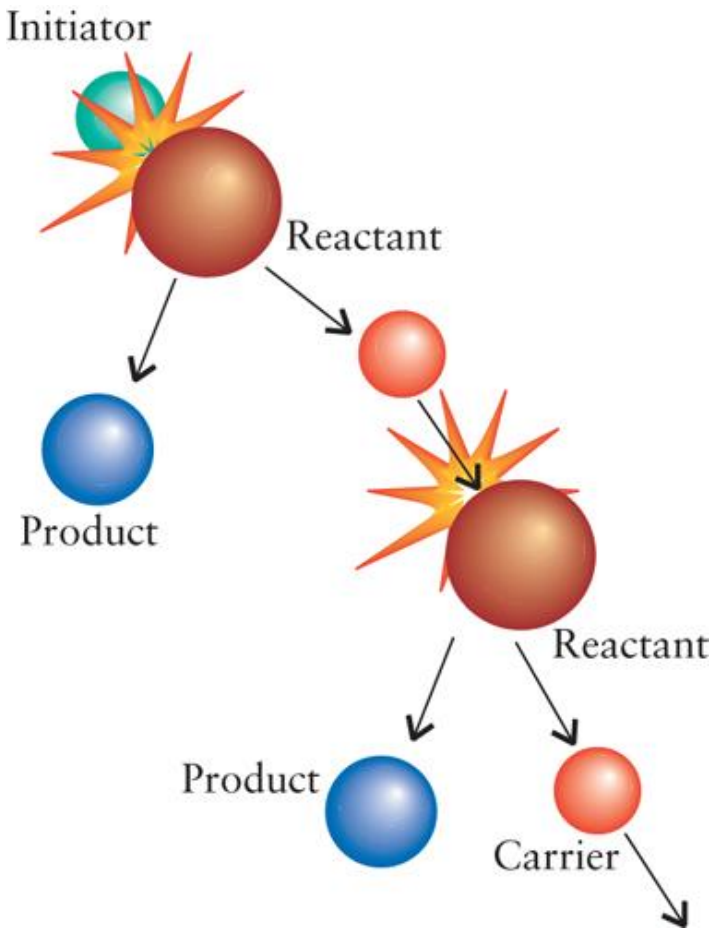
Chain Reactions

Chain reactions have highly reactive intermediates that produce more highly reactive intermediates…and so on.

In these reactions an intermediate compound is called a chain carrier.

Radical chain reaction have radical intermediates.

The rate laws are very complex, and not derived here.



Chain Reactions

Formation of HBr in the reaction takes place by a chain reaction.

H_2 (g) + Br_2 (g) $\rightarrow$ 2 HBr(g)

The first step called, **intiation**, produces chain carriers H· and Br·, Δ is heat *hυ* is light.

Br_2 (g) $\xrightarrow{\Delta \; or \; h\upsilon}$ Br· + Br·

The second step, **propagation**, creates more chain carriers, in this case radicals.

Br· + H_2 $\rightarrow$ HBr + H·
H· + Br_2 $\rightarrow$ HBr + Br·

The final step, **termination**, occures when two chain carriers combine to form products.

Br· + Br· $\rightarrow$ Br_2
H· + Br· $\rightarrow$ HBr

Rates & Equilibrium

The equilibrium constant for an elementary reaction is equal to the forward rate constants of the reaction divided by the reverse rate constant:

For $A + B \rightleftharpoons C + D$ Rate = $k_1[A][B]$

$C + D \rightleftharpoons A + B$ Rate = $k_{-1}[C][D]$

$\text{Rate}_{\text{forward}} = \text{Rate}_{\text{reverse}}$

$k_1[A][B] = k_{-1}[C][D]$

Or $\frac{k_1}{k_{-1}} = \frac{[C][D]}{[A][B]}$

$$K = \frac{k_1}{k_{-1}}$$

So for multiply steps we get $K = \frac{k_1}{k_{-1}} \times \frac{k_2}{k_{-2}} \ldots$

Effect of Temperature

We've seen how rates depend on concentrations.

Rates also depend on temperature. An ***increase of 10°C*** from room temperature typically ***doubles the rate*** of organic reactions.

One of the reasons why we put food in the refrigerator, to keep it from spoiling or why you get a fever.

Rates almost always increase with temperature.

magnesium in cold water magnesium in hot water

Effect of Temperature

Arrhenius equation

$$\ln k = \ln A - \frac{E_a}{RT} \qquad \text{or} \qquad k = Ae^{-E_a/RT}$$

The two constants, **A** and **E_a**, are known as the Arrhenius parameters for the reaction and are found from experiment.

A is called the **pre-exponential factor**.

E_a is the **activation energy**.

Both A and E_a are <u>nearly independent of temperature</u> but have values that depend on the reaction being studied.

Effect of Temperature

Activation Energy (E_a): The minimum energy that we need to start a reaction.

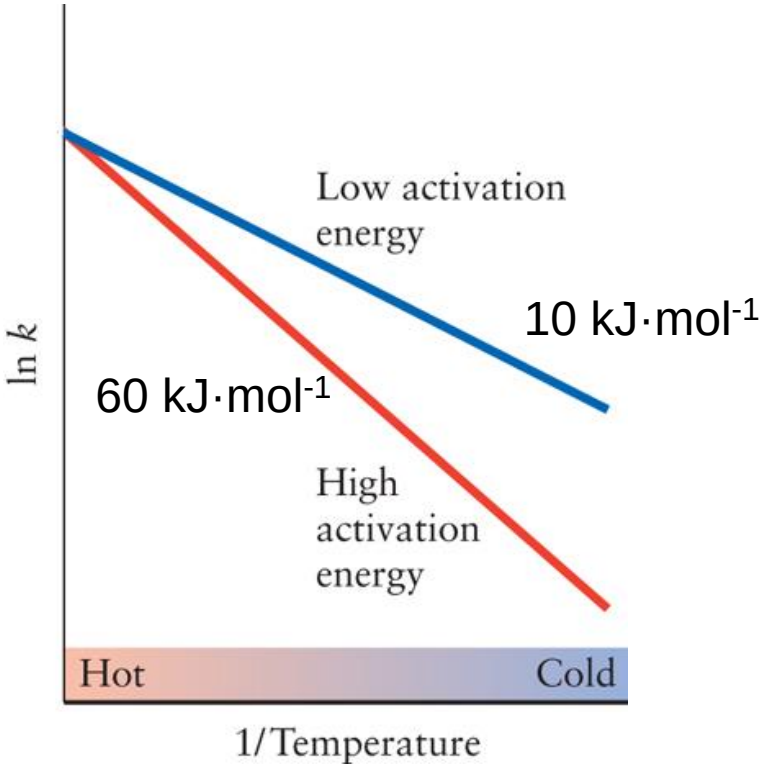
$$\ln k = -\frac{E_a}{R}\left(\frac{1}{T}\right) + \ln A$$

y-intercept = slope + b

E_a and temperatures are closely tied to each other.

Low E_a, 10 kJ·mol^{-1}, have a low slope, and are not so entirely dependent on temperature.

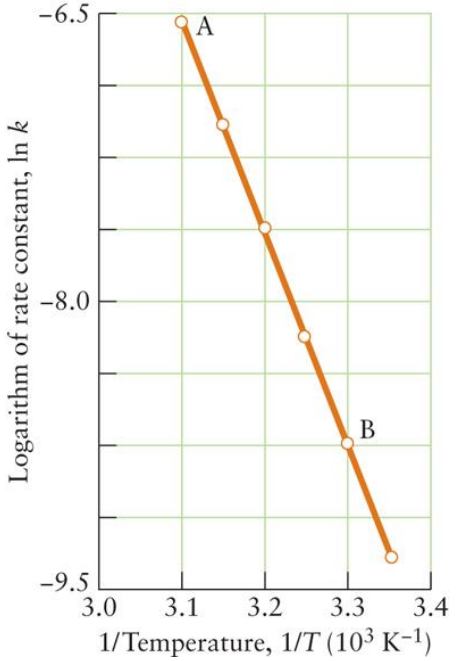
High E_a, above 60 kJ·mol^{-1}, produce a steep slope, and temperature dependent reactions.



Example 7: The rate constant for the second-order reaction between bromoethane and hydroxide ions in water,
$C_2H_5Br(aq) + OH^-(aq) \rightarrow C_2H_5OH(aq) + Br^-(aq)$, was measured at several temperatures, with the results shown here:

The first step is to make a table, a computerized spread sheet works best, to find (1) the temperature in Kelvin, (2), 1/T, (3) ln k, and (4) find the slope either by graph or spreadsheet.

$$\ln k = \ln A - \frac{E_a}{R}\left(\frac{1}{T}\right)$$



Temp °C	25	30	35	40	45	50
$k \times 10^{-3}$ ($L \cdot mol^{-1} \cdot s^{-1}$)	8.80E-05	1.60E-04	2.80E-04	5.00E-04	8.50E-04	1.40E-03
T (K)	2.98E+02	3.03E+02	3.08E+02	3.13E+02	3.18E+02	3.23E+02
$1/T \times 10^{-3}$ (K^{-1})	3.35E-03	3.30E-03	3.25E-03	3.19E-03	3.14E-03	3.09E-03
ln k	-9.34E+00	-8.74E+00	-8.18E+00	-7.60E+00	-7.07E+00	-6.57E+00
slope	-10698.8					

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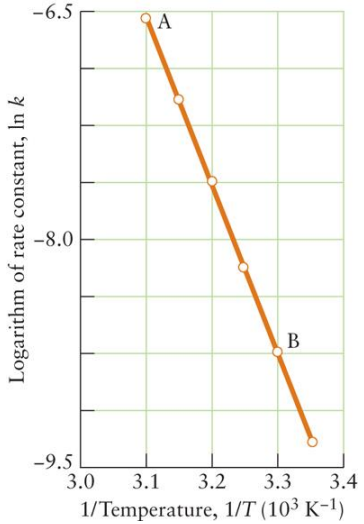


The slope is = $-E_a/R$, or $E_a = -R \times m$,

Here the slope = -1.07×10^4 K

$E_a = -R \times m$, $-(8.3145\ J \cdot K^{-1} \cdot mol^{-1})\ (-1.07 \times 10^4\ K) = 8.9 \times 10^4\ J \cdot mol^{-1}$

$= 89\ kJ \cdot mol^{-1}$

Effect of Temperature

Arrhenius equation

At two different temperatures and two different k's:

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

Example 8: The hydrolysis of sucrose is a part of the digestive process. To investigate how strongly the rate depends on our body temperature, calculate the rate constant for the hydrolysis of sucrose at 35.0°C, given that k = 1.0 $mL \cdot mol^{-1} \cdot s^{-1}$ at 37.0°C (normal body temperature) and that the activation energy of the reaction is 108 $kJ \cdot mol^{-1}$.

We're asked to solve for k_2, so we use

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

108 $kJ \cdot mol^{-1}$ = 108,000 $J \cdot mol^{-1}$
35.0°C+ 273.15 = 308.2K
37.0°C + 273.15 = 310.5K
k_1 = 1.0 $mL \cdot mol^{-1} \cdot s^{-1}$ at 37.0°C, T_1 = 310.5K
(keeping 1's and 2's together)

Example 8: The hydrolysis of sucrose is a part of the digestive process. To investigate how strongly the rate depends on our body temperature, calculate the rate constant for the hydrolysis of sucrose at 35.0°C, given that k = 1.0 $mL \cdot mol^{-1} \cdot s^{-1}$ at 37.0°C (normal body temperature) and that the activation energy of the reaction is 108 $kJ \cdot mol^{-1}$.

The right side, $-\frac{E_a}{R}\left(\frac{1}{T_2}-\frac{1}{T_1}\right)$, $-\frac{108{,}000\ J \cdot mol^{-1}}{8.3145\ J \cdot K^{-1} \cdot mol^{-1}}\left(\frac{1}{308.2K}-\frac{1}{310.5K}\right)$

$= -0.27$

From Ln x = A $\rightarrow$ x = e^A, $\frac{k_2}{k_1} = e^{-0.27}$,

$\frac{k_2}{1.0\ mL \cdot mol^{-1} \cdot s^{-1}} = e^{-0.27}$, $k_2 = 0.76\ mL \cdot mol^{-1} \cdot s^{-1}$

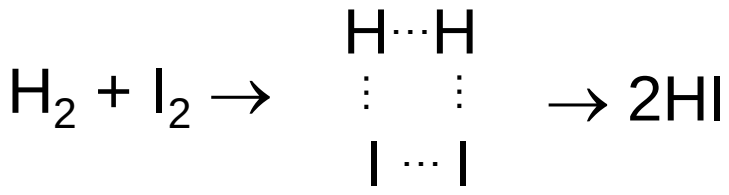
the high E_a means it is temperature sensitive.

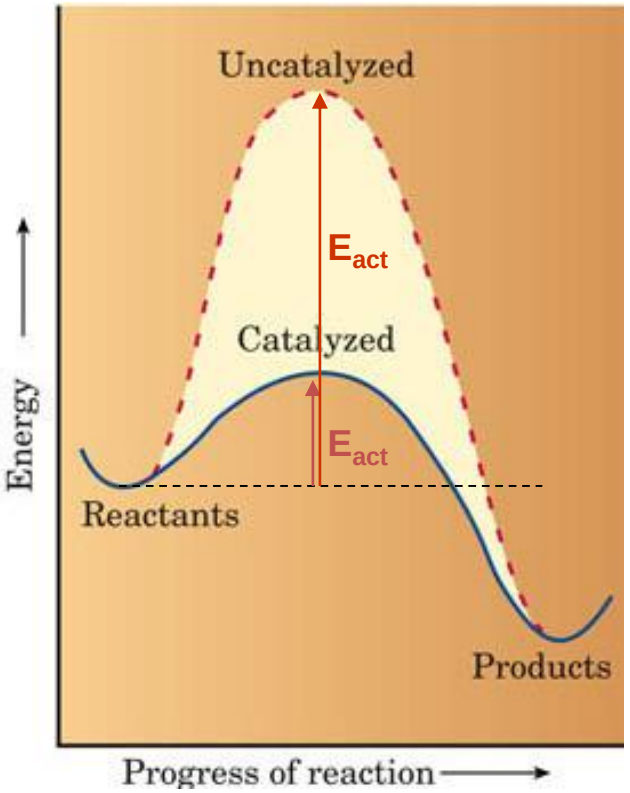
Catalyst

- Like a catalyst, they increase the rate of the reactions (such as biological reactions).

- But, they are not changed at the end of the reaction.

- Lower the activation energy for the reaction.





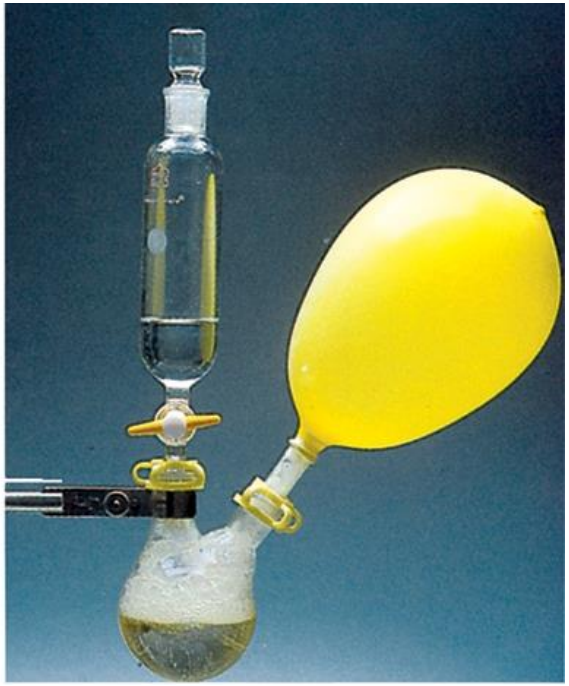
- Less energy is required to convert reactants to products.

Homogenous Catalyst

A homogeneous catalyst are in the same phase as the reactants.

Peroxide can be stored safely for months but adding a catalyst, Br_2, causes rapid decomposition:

$$2H_2O_2\,(ag) \rightarrow 2H_2O(l) + O_2(g) \text{ rapidly.}$$



Heterogeneous Catalyst

Catalyst in a different phase the reactants.

Common heterogeneous catalysts are finely divided or porous solids that have a large surface area.

A common one is the iron catalyst used in the Haber process for ammonia.

Example 9: How does a catalyst affect (a) the rate of the reverse reaction; (b) ΔH for the reaction ?

Answer: (a) Increases it; (b) has no effect

Example 10: How does a homogeneous catalyst affect (a) the rate law; (b) the equilibrium constant ?

Answer: (a) since a catalysts changes the pathway it will change the rate law and it will appears in it; (b) catalysts have no effect on any thermodynamic variable so it has no effect.

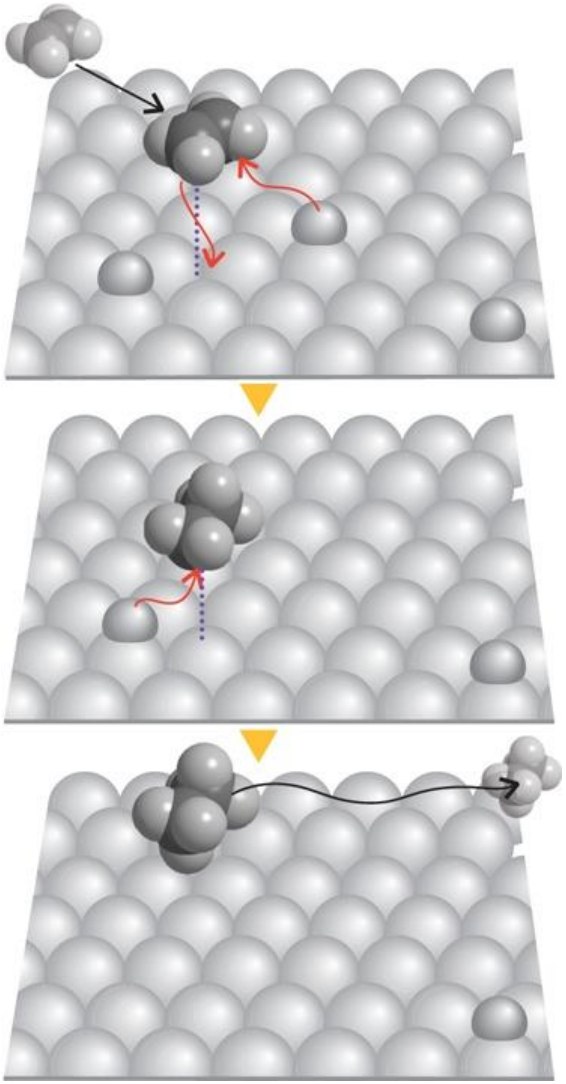
How does a catalyst lower the E_a?

A reaction between ethene, $CH_2=CH_2$, and hydrogen on a Pt metal catalytic surface.

The ethene and hydrogen **stick** to the metal surface (adsorb).

The **metals dissociates the hydrogen**.

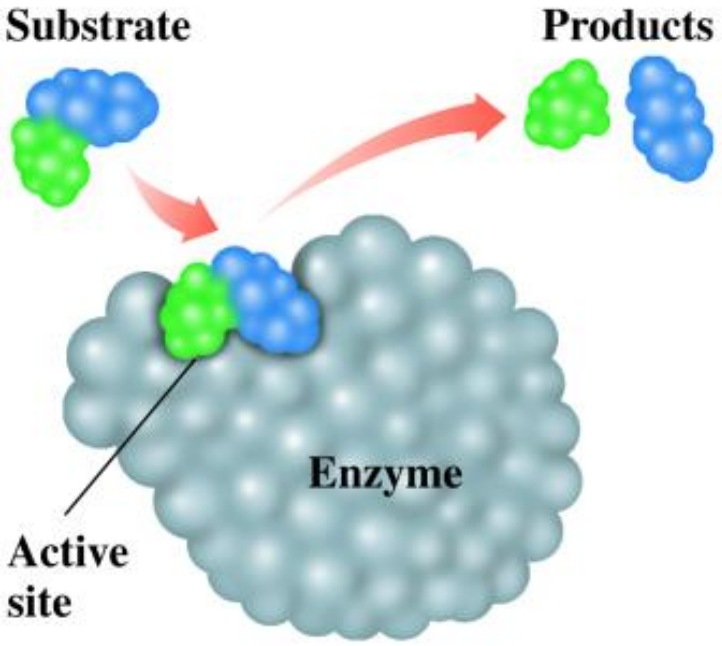
The ethene molecule meets two hydrogen atoms to form bonds making CH_3CH_3; ethane is formed and escapes from the surface.



Enzymes

Living cells contain thousands of different kinds of catalysts.

We call them Enzymes.



Enzyme: globular protein