Chapter 19: Chemical Kinetics

Key topics:
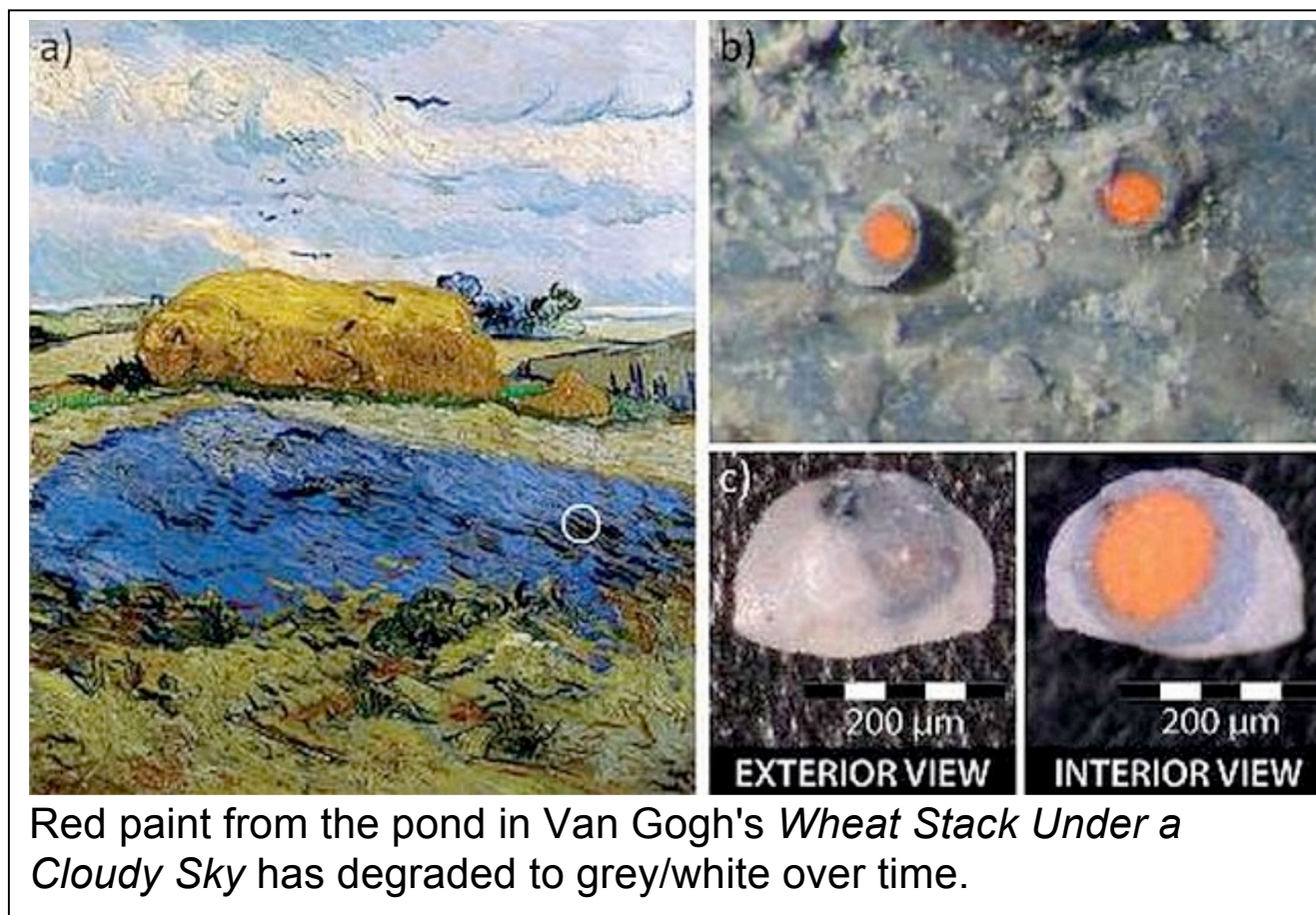***Reaction Rates***
Factors That Affect Reaction Rates
Reaction Mechanisms

How fast does a reaction occur?
e.g., many famous painting are changing color…

Red paint from the pond in Van Gogh's *Wheat Stack Under a Cloudy Sky* has degraded to grey/white over time.
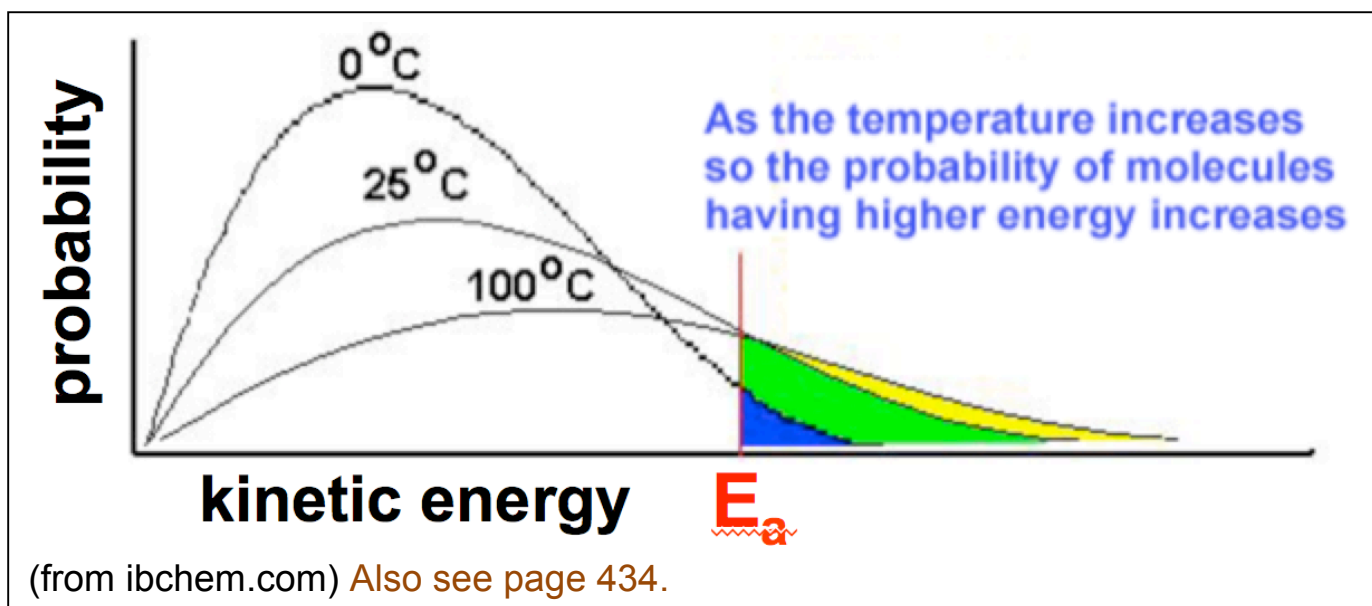
Collision Theory of Chemical Reactions

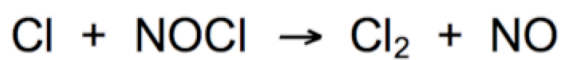A very simple picture of a chemical reaction between two molecules is that
1. They must collide with enough energy to react
2. They must collide in the correct orientation to react

The collision (kinetic energy) can be transferred into vibrational energy, which can lead to bond breaking. This is the first step in a chemical reaction.
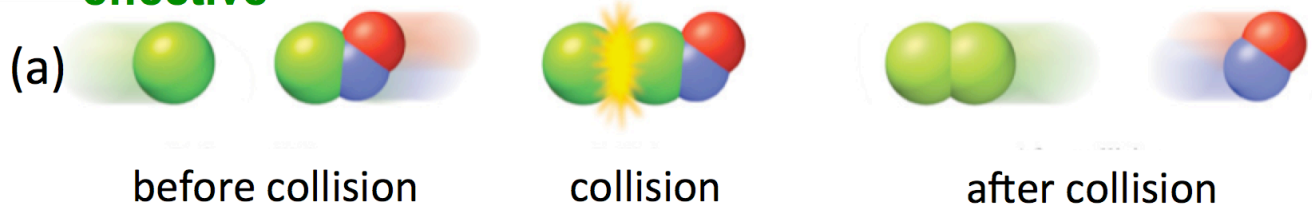
The minimum energy required to initiate a reaction is called the **activation energy**, E_a. If the collision is $< E_a$, it is ineffective and the reactants simply bounce off each other. Temperature has a large effect on having energy $> E_a$.

(from ibchem.com) Also see page 434.

The correct orientation is also needed for an effective reaction:

$$Cl + NOCl \rightarrow Cl_2 + NO$$

effective

(a)

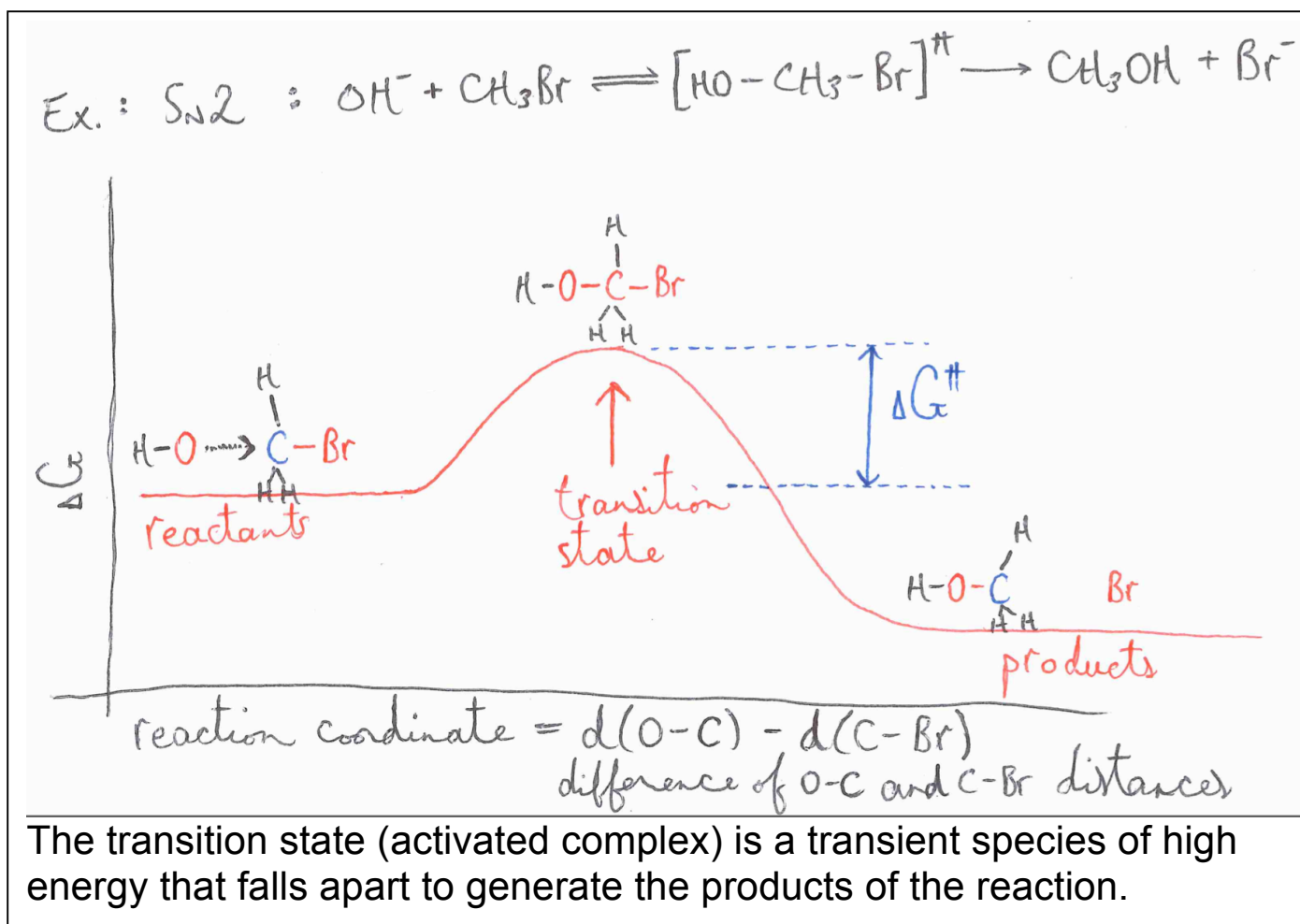before collision   collision   after collision

ineffective

(b)

Orientation dependence on a simple reaction.

Transition state theory (TST), also known as Activated Complex Theory, is a more sophisticated theory that has two main assumptions
 1) The transition state is in equilibrium with the reactions.
  2) One (special) vibrational motion results in the breakup of the transition state into the products.

Ex.: S_N2 : $OH^- + CH_3Br \rightleftharpoons [HO-CH_3-Br]^{\ddagger} \longrightarrow CH_3OH + Br^-$

reaction coordinate = $d(O-C) - d(C-Br)$
difference of O-C and C-Br distances

The transition state (activated complex) is a transient species of high energy that falls apart to generate the products of the reaction.

Measuring Reaction Progress & Expressing Reaction Rate

We can express the reaction rate as either:
  o Rate of disappearance of reactants (decrease or –ve)
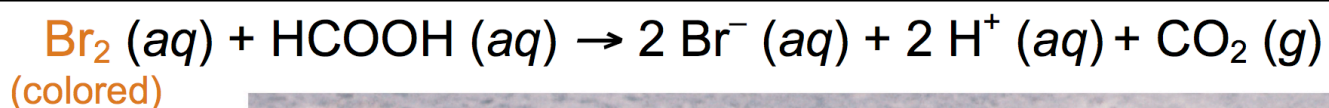 o Rate of appearance of products (increase or +ve)
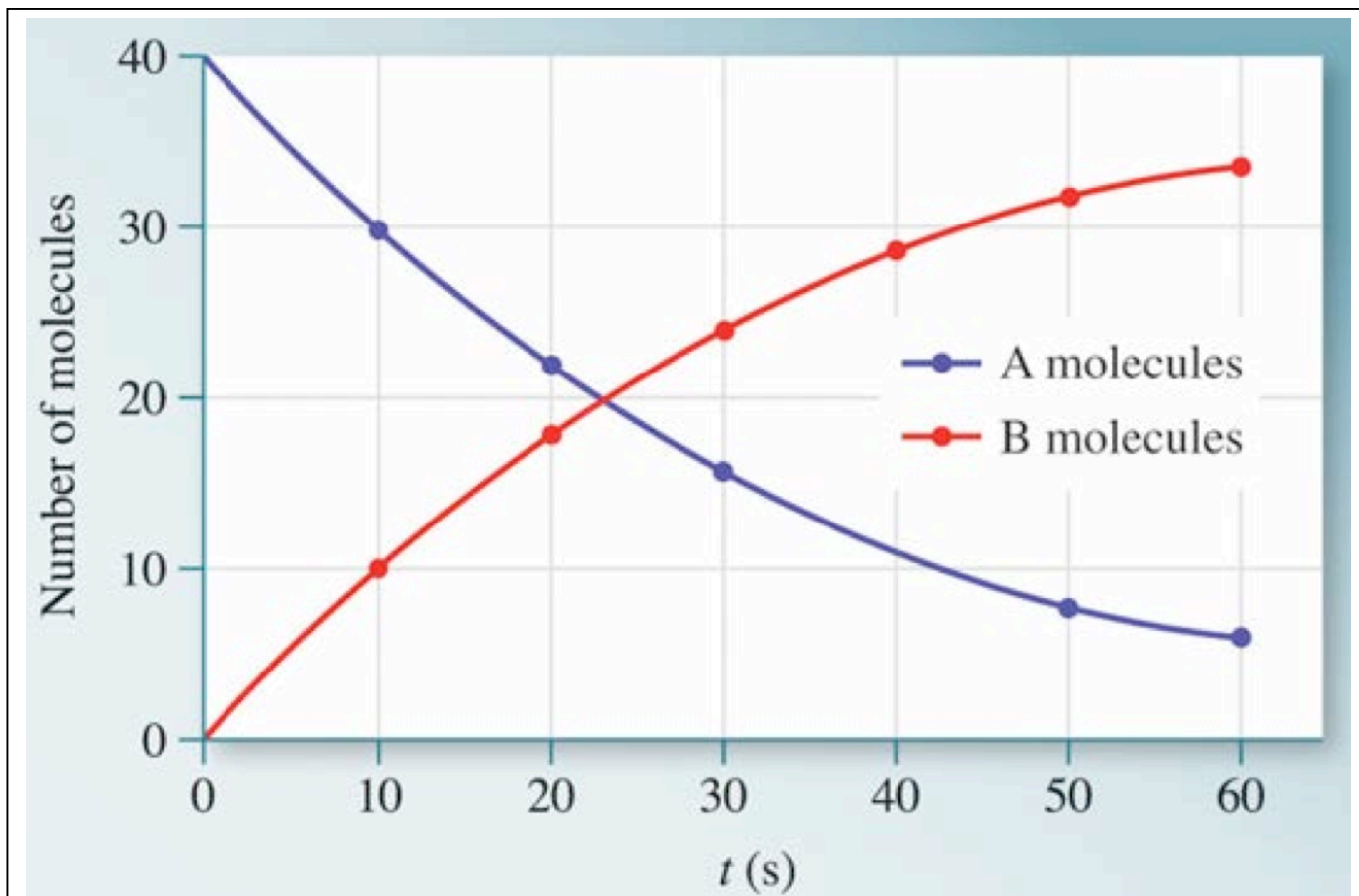
Reaction progress with time. The rate changes over time.

We can follow a color change, conductance change, pressure change, or whatever is convenient.
Consider the reaction   A → B.

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

Br$_2$ (aq) + HCOOH (aq) → 2 Br$^-$ (aq) + 2 H$^+$ (aq) + CO$_2$ (g)
(colored)

Reaction progress can be monitored using a spectrometer.

$$\text{average rate} = -\frac{\Delta[Br_2]}{\Delta t} = -\frac{[Br_2]_{\text{final}} - [Br_2]_{\text{initial}}}{t_{\text{final}} - t_{\text{initial}}}$$

The average rate decreases over time (see Table 19.1).

The **instantaneous rate** is given by the tangent line:

Rate at 100 s:
2.96×10^{-5} M/s

Rate at 200 s:
2.09×10^{-5} M/s

Rate at 300 s:
1.48×10^{-5} M/s

The instantaneous rate is given by the tangent line.
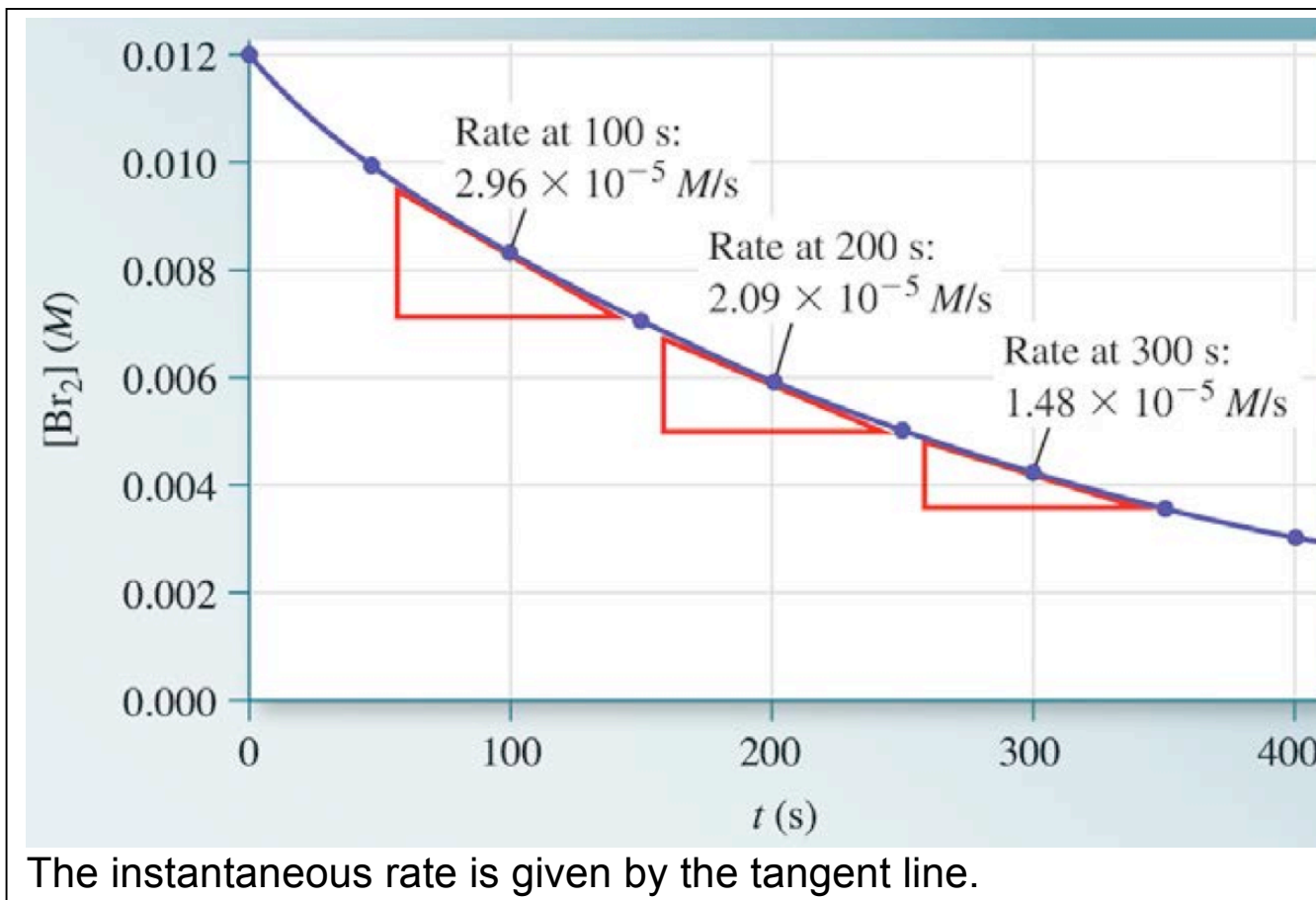
From Table 19.1:

Time (s)	$[Br_2]$	Rate (M/s)
50	0.0101	3.52×10^{-5}
250	0.00500	1.75×10^{-5}

We can see that when $[Br_2]$ is halved, the rate is halved.
Therefore rate $\propto [Br_2]$, or rate = k $[Br_2]$ where k is the
proportionality constant.
k = rate constant (does depend on the temperature)

Value of k? $k = $ rate / $[Br_2]$

at $t = 50$ s, $k = \dfrac{3.52 \times 10^{-5} M s^{-1}}{0.0101 \, M} = 3.49 \times 10^{-3} \, s^{-1}$

at $t = 250$ s, $k = \dfrac{1.75 \times 10^{-5} M s^{-1}}{0.00500 \, M} = 3.50 \times 10^{-3} \, s^{-1}$

(same within experimental error)

Consider the reaction   A → 2B.

$$\text{rate} = -\dfrac{\Delta[A]}{\Delta t} = \dfrac{1}{2}\dfrac{\Delta[B]}{\Delta t}$$

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

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

e.g., Write the balanced equation corresponding to the following rate expression

$$\text{rate} = -\dfrac{1}{2}\dfrac{\Delta[N_2O_5]}{\Delta t} = \dfrac{1}{2}\dfrac{\Delta[N_2]}{\Delta t} = \dfrac{1}{5}\dfrac{\Delta[O_2]}{\Delta t}$$

Solution:
-ve sign indicates reactants and +ve sign indicates products.

So this reaction should be: $2N_2O_5 \rightarrow 2N_2 + 5O_2$
We should double check that the reaction is balanced.

e.g., Consider the following unbalanced equation: A + B → C.
When C is being formed at the rate of 0.086 M/s, A is being consumed at a rate of 0.172 M/s, and B at 0.258 M/s. Balance the equation from this information.

Solution:

We are told that $\dfrac{\Delta[C]}{\Delta t} = 0.086$, $\dfrac{\Delta[A]}{\Delta t} = -0.172$, $\dfrac{\Delta[B]}{\Delta t} = -0.258$

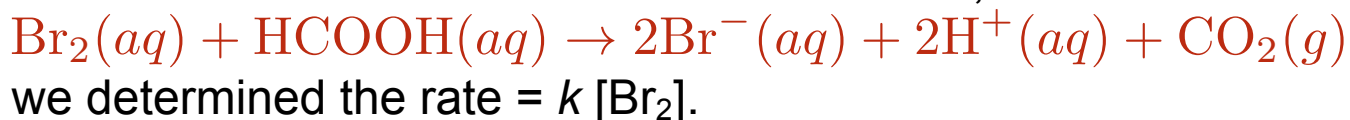If we write the balanced equation *a*A + *b*B → *c*C, we know that

$$-\frac{1}{a}\frac{\Delta[A]}{\Delta t} = -\frac{1}{b}\frac{\Delta[B]}{\Delta t} = \frac{1}{c}\frac{\Delta[C]}{\Delta t} \quad \text{or} \quad \frac{0.172}{a} = \frac{0.258}{b} = \frac{0.086}{c}$$

If we divide each expression by 0.086 we get

$$\frac{2}{a} = \frac{3}{b} = \frac{1}{c}$$ Therefore *a* = 2, *b* = 3, and *c* = 1.

Dependence of Reaction Rate on Reactant Concentration

In the bromine reaction we considered earlier,
$$\mathrm{Br_2}(aq) + \mathrm{HCOOH}(aq) \rightarrow 2\mathrm{Br}^-(aq) + 2\mathrm{H}^+(aq) + \mathrm{CO_2}(g)$$
we determined the rate = *k* [Br$_2$].

In terms of the reactant concentrations, we write
$$\mathrm{rate} = k[\mathrm{Br_2}]^x + [\mathrm{HCOOH}]^y$$
with x = 1 and y = 0. The exponents (x and y) are **empirically** determined. Without experimental data we can't simply predict their values.

In general, for $aA + bB \rightarrow cC + dD$, the rate law is
$$\mathrm{rate} = k[\mathrm{A}]^x[\mathrm{B}]^y.$$

➤ x = 0: the reaction is 0th order with respect to A.
➤ x = 1: the reaction is 1st order with respect to A.
➤ x = 2: the reaction is 2nd order with respect to A.

The overall reaction order is the sum of the exponents, so the bromine reaction is 1st order overall (1 + 0 = 1).

To determine the rate law, we often analyze <u>initial rate</u> data from experiments. (The initial rate is the instantaneous rate at the beginning of the reaction.)

For the reaction $F_2(g) + 2ClO_2(g) \rightarrow 2FClO_2(g)$ we have the following experimental data:

TABLE 19.2	Initial Rate Data for the Reaction Between F_2 and ClO_2		
Experiment	$[F_2]$ (M)	$[ClO_2]$ (M)	Initial rate (M/s)
1	0.10	0.010	1.2×10^{-3}
2	0.10	0.040	4.8×10^{-3}
3	0.20	0.010	2.4×10^{-3}

We know the rate law must be $\text{rate} = k[F_2]^x[ClO_2]^y$.
Comparing exp. 1 and 3,

$$\frac{\text{rate}_3}{\text{rate}_1} = \frac{k[F_2]^x[ClO_2]^y}{k[F_2]^x[ClO_2]^y} = \frac{2.4 \times 10^{-3}\,Ms^{-1}}{1.2 \times 10^{-3}\,Ms^{-1}} = \frac{k[0.20]^x[0.010]^y}{k[0.10]^x[0.010]^y}$$
$$\Rightarrow 2 = 2^x \Rightarrow x = 1$$

Comparing exp. 1 and 2,
$$\frac{\text{rate}_2}{\text{rate}_1} = \frac{k[F_2]^x[ClO_2]^y}{k[F_2]^x[ClO_2]^y} = \frac{4.8 \times 10^{-3}\,Ms^{-1}}{1.2 \times 10^{-3}\,Ms^{-1}} = \frac{k[0.10]^x[0.040]^y}{k[0.10]^x[0.010]^y}$$
$$\Rightarrow 4 = 4^y \Rightarrow y = 1$$

Therefore we have

$$\text{rate} = k[F_2]^1[ClO_2]^1 \qquad (2^{\text{nd}} \text{ order overall})$$

Then we can determine k from any single exp.

$$k = \frac{\text{rate}}{[\text{F}_2][\text{ClO}_2]} = \frac{2.4 \times 10^{-3}\,M\text{s}^{-1}}{[0.20\,M][0.010\,M]} = 1.2\,M^{-1}\text{s}^{-1}$$

The rate has units of $M\,\text{s}^{-1}$, so k has units as follows:

TABLE 19.4	Units of the Rate Constant k for Reactions of Various Overall Orders	
Overall reaction order	**Sample rate law**	**Units of k**
0	rate $= k$	$M \cdot \text{s}^{-1}$
1	rate $= k[\text{A}]$ or rate $= k[\text{B}]$	s^{-1}
2	rate $= k[\text{A}]^2$, rate $= k[\text{B}]^2$, or rate $= k[\text{A}][\text{B}]$	$M^{-1} \cdot \text{s}^{-1}$
3*	rate $= k[\text{A}]^2[\text{B}]$ or rate $= k[\text{A}][\text{B}]^2$	$M^{-2} \cdot \text{s}^{-1}$

*Another possibility for a third-order reaction is rate $= k[\text{A}][\text{B}][\text{C}]$, although such reactions are very rare.

Note:
  ➢ rate law defined in terms of reactants only
  ➢ exponents are usually positive whole numbers or zero
      ▪ can be negative (inhibitor)
      ▪ can be a fraction (won't see in this course)

e.g., For the reaction A + B → 2C, the rate = $k[A]^2$ with k = 1.3 × 10^{-2} M^{-1} s^{-1}. Fill in the missing table entries:

Experiment	[A] (*M*)	[B] (*M*)	Initial rate (*M*/s)
1	0.013	0.250	2.20 × 10^{-6}
2	0.026	0.250	
3		0.500	2.20 × 10^{-6}

Solution:
Blue entry: the rate is the same as exp. 1, so [A] must be the same as exp. 1 since this is what the rate depends on.

Green entry: since [A] doubles from exp. 1, the rate must be 2^2 = 4 times the rate of exp. 1 = 8.80 × 10^{-6}.

Dependence of Reaction Concentration on Time

How do the reactant (and product) concentrations change with time? Analyze this in terms of the overall reaction order.

First Order Reactions

A first order reaction depends on the concentration of one of the reactants raised to the first power. We will write such a reaction as aA → products.

$$\text{rate} = -\frac{1}{a}\frac{\Delta[A]}{\Delta t} = k[A] \quad \Rightarrow \quad -\frac{\Delta[A]}{\Delta t} = (ak)[A] = k^*[A]$$

where we have redefined the rate constant to include the stoichiometric coefficient. Now we change Δ to d (finite change to infinitesimal change) and just write k for k^*

$$-\frac{d[A]}{dt} = k[A] \quad \Rightarrow \quad \frac{d[A]}{[A]} = -k\,dt \quad \text{or} \quad \frac{1}{[A]}d[A] = -k\,dt$$

and integrate from $t = 0$ to $t = t$

$$\int_{[A]_0}^{[A]_t} \frac{1}{[A]} d[A] = -k \int_0^t dt$$

which gives the first order integrated rate law

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

e.g., For 2A → B, k = 7.5 × 10^{-3} s^{-1}.
With [A]$_0$ = 2.25 *M*, find [A] after 2 minutes.

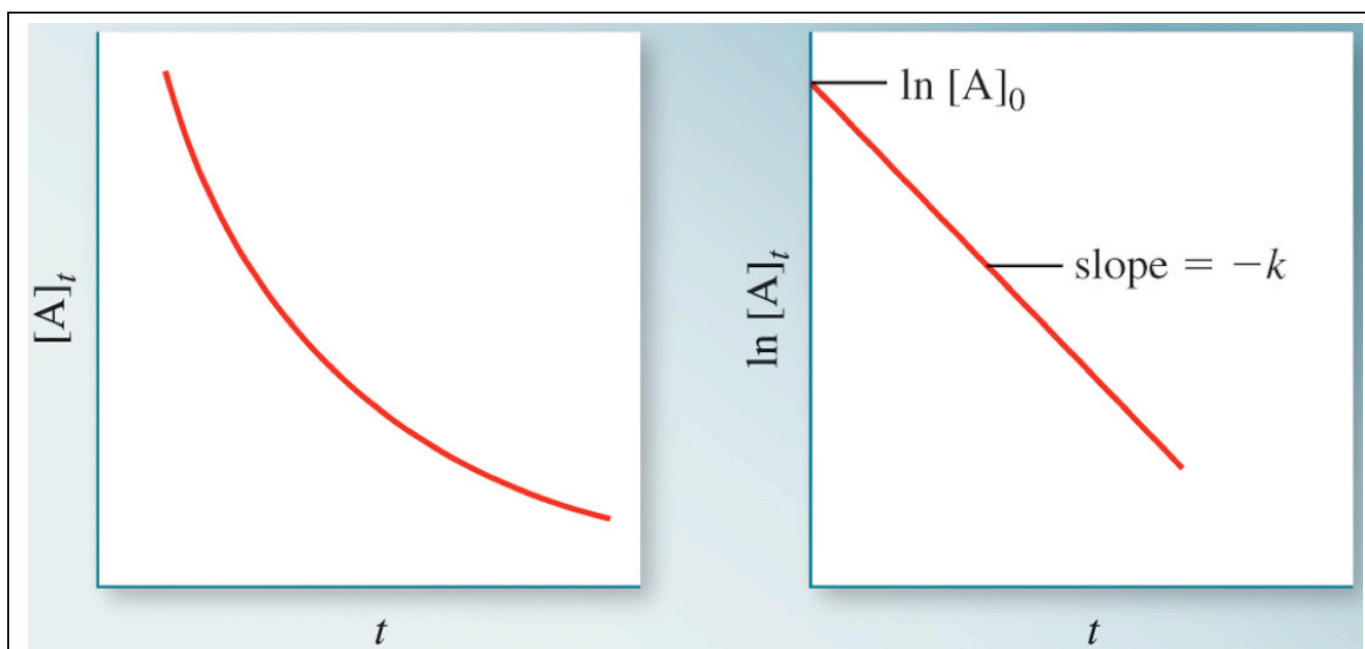Solution:
2 minutes = 120 s, so

$$[A]_t = [A]_0 e^{-kt} = (2.25\,M)e^{-0.9} = 0.91\,M$$

From concentration vs. time data (*e.g.* Lab 17 in Chem 1112) we would do the following:

$$\underbrace{\ln[A]_t}_{y} = \underbrace{-k}_{m}\underbrace{t}_{x} + \underbrace{\ln[A]_0}_{b}$$

First order kinetics; we obtain a straight line when the data is plotted on a logarithmic scale.

Half-life: The half-life of a reaction ($t_{1/2}$) is the time required for the reactant concentration to drop to half of its original value. We express this as
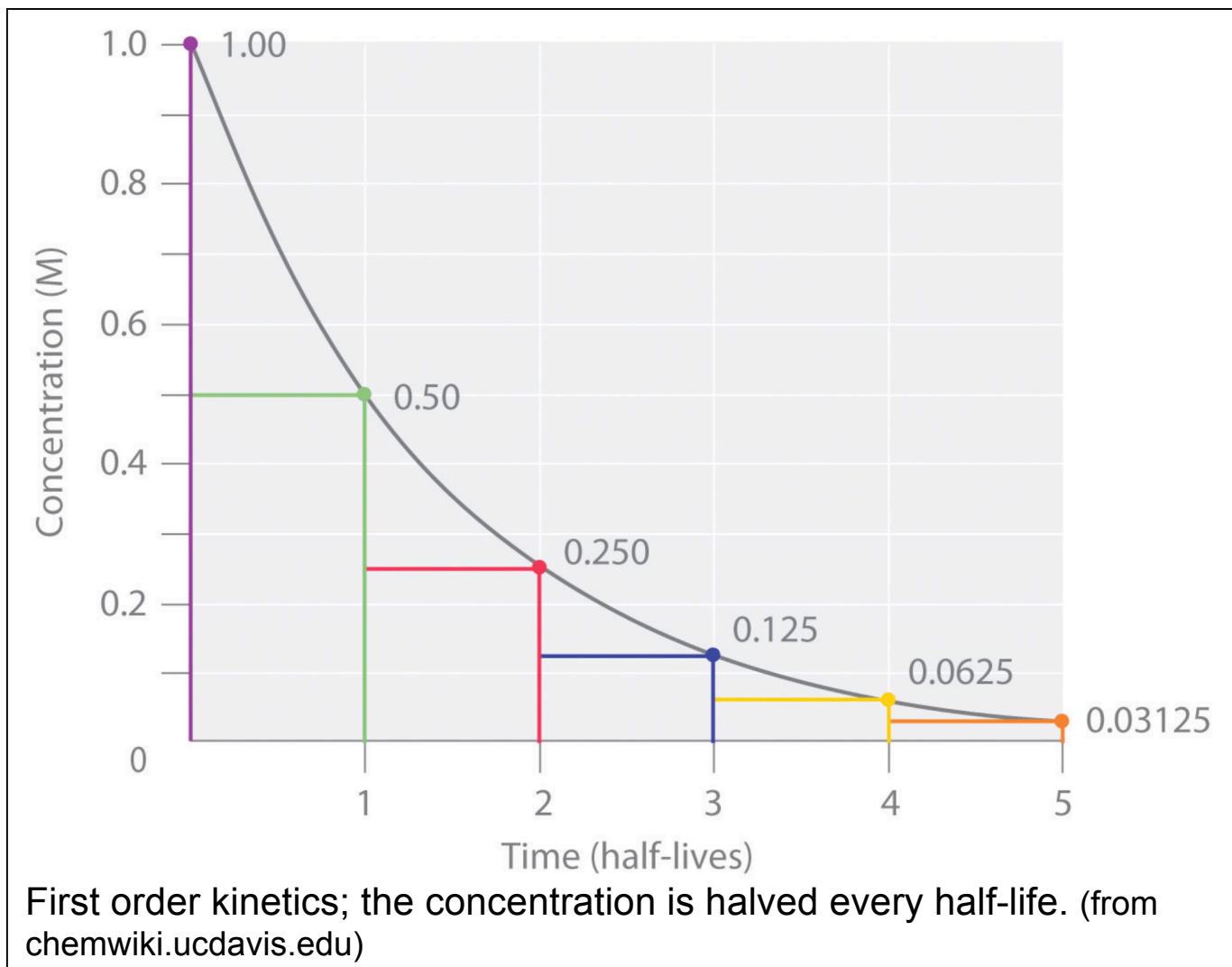
$$[A]_t = [A]_{t_{1/2}} = \frac{[A]_0}{2} \implies \frac{[A]_{t_{1/2}}}{[A]_0} = \frac{1}{2}$$

Then the integrated rate law gives

$$\ln\frac{[A]_{t_{1/2}}}{[A]_0} = \ln\frac{1}{2} = -kt_{1/2}$$

$$\ln \frac{1}{2} = -\ln 2 \approx -0.693 \ \text{ so that } \ t_{1/2} = \frac{0.693}{k}$$

First order kinetics; the concentration is halved every half-life. (from chemwiki.ucdavis.edu)

e.g., Calculate the rate constant for the first order decay of ^{24}Na ($t_{1/2}$ = 14.96 hours).

Solution:

$$14.96\,\text{h} = \frac{0.693}{k} \ \Rightarrow \ k = \frac{0.693}{14.96\,\text{h}} = 4.63 \times 10^{-2}\,\text{h}^{-1} \ \left(\times \frac{24\,\text{h}}{1\,\text{day}} = 1.11\,\text{day}^{-1} \right)$$

e.g., The decomposition of H_2O_2 is first order:
$H_2O_2 \rightarrow H_2O + \frac{1}{2} O_2$ with $k = 7.00 \times 10^{-4}$ s^{-1} and $[H_2O_2]_0 =$ 0.100 *M*. How long will it take for $[H_2O_2] = 0.0370$ *M*?

Solution:

$$\ln \frac{[A]_t}{[A]_0} = -kt \Rightarrow t = -\frac{1}{k} \ln \frac{[A]_t}{[A]_0} = -\frac{1}{7 \times 10^{-4} \text{ s}^{-1}} \ln \frac{0.0370 \, M}{0.100 \, M}$$
= 1420 s = 23.7 min.

Second Order Reactions

For A + B → C,
A second order reaction looks like either
   1) rate = $k[A]^2$
   2) rate = $k[A][B]$

We will only consider case 1).
Similar to the first order case, we redefine the rate constant to include the stoichiometric coefficient. We write

$$\text{rate} = -\frac{\Delta[A]}{\Delta t} = k[A]^2$$
Now we change Δ to *d* (finite change to infinitesimal change):

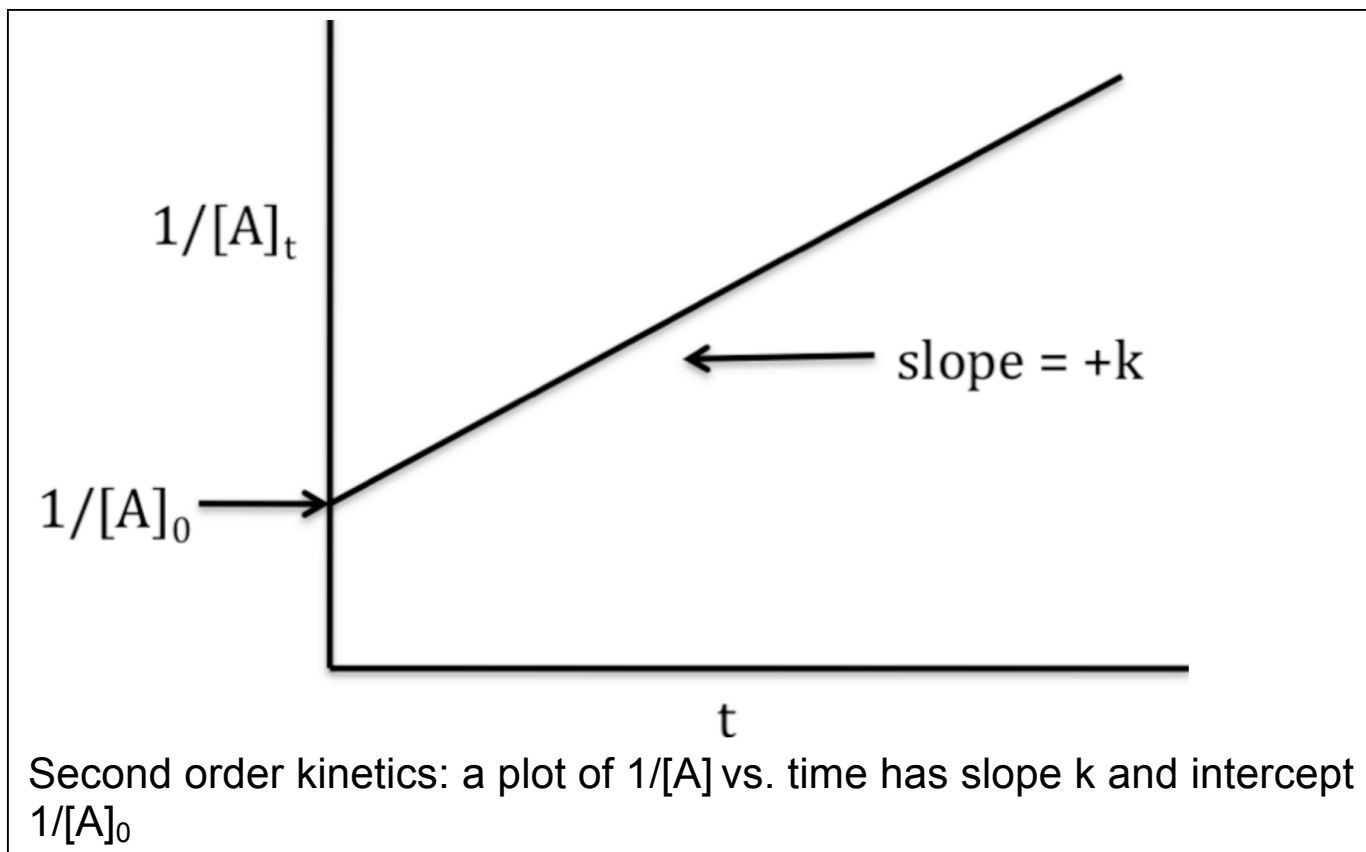$$-\frac{d[A]}{dt} = k[A]^2 \Rightarrow \frac{1}{[A]^2} d[A] = -k \, dt$$

Then we integrate from $t = 0$ to $t = t$

$$\int_{[A]_0}^{[A]_t} \frac{1}{[A]^2} d[A] = -k \int_0^t dt \Rightarrow -\frac{1}{[A]_t} + \frac{1}{[A]_0} = -kt$$

and rearrange

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

Second order kinetics: a plot of 1/[A] vs. time has slope k and intercept $1/[A]_0$

To compute the half-life, we use $[A]_t = [A]_{t_{1/2}} = [A]_0/2$

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

e.g., The reaction 2A → B is second order in A with k = 32 M^{-1} s^{-1}. (a) With $[A]_0$ = 0.0075 M, how long does it take for [A] to drop to 0.0018 M? Calculate the half-life of the reaction for $[A]_0$ = 0.0075 M and for $[A]_0$ = 0.0025 M.

Solution:

$$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0} \quad \Rightarrow \quad kt = \frac{1}{[A]_t} - \frac{1}{[A]_0} \quad \Rightarrow \quad t = \frac{1}{k[A]_t} - \frac{1}{k[A]_0}$$

$$t = \frac{1}{(32\,M^{-1}s^{-1})(0.0018\,M)} - \frac{1}{(32\,M^{-1}s^{-1})(0.0075\,M)} = 17.36\,s - 4.17\,s$$

=13.2 s. For the half-life,

$$t_{1/2} = \frac{1}{(32\,M^{-1}s^{-1})(0.0075\,M)} = 4.17\,s$$

$$t_{1/2} = \frac{1}{(32\,M^{-1}s^{-1})(0.0025\,M)} = 12.5\,s$$

Zeroth Order Reactions

A zeroth order reaction is independent of reactant concentration: For aA → products, rate = $k[A]^0$ = k.

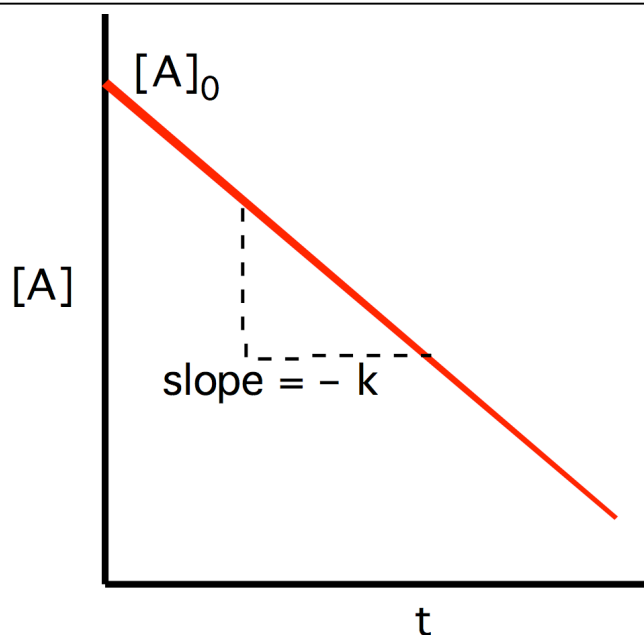Once again, we redefine the rate constant to include the stoichiometric coefficient and write

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

Now we change Δ to d (finite change to infinitesimal change):

$$-\frac{d[A]}{dt} = k \quad \Rightarrow \quad d[A] = -k\,dt$$

Then we integrate from $t = 0$ to $t = t$

$$\int_{[A]_0}^{[A]_t} d[A] = -k \int_0^t dt \quad \Rightarrow \quad [A]_t - [A]_0 = -kt \ \text{ or } \ [A]_t = -kt + [A]_0$$

A plot of [A] versus time yields a straight line with slope -*k* and intercept $[A]_0$

TABLE 19.5	Summary of the Kinetics of Zeroth-Order, First-Order, and Second-Order Reactions		
Order	Rate law	Integrated rate law	Half-Life
0	rate $= k$	$[A]_t = -kt + [A]_0$	$\dfrac{[A]_0}{2k}$
1	rate $= k[A]$	$\ln\dfrac{[A]_t}{[A]_0} = -kt$	$\dfrac{0.693}{k}$
2	rate $= k[A]^2$	$\dfrac{1}{[A]_t} = kt + \dfrac{1}{[A]_0}$	$\dfrac{1}{k[A]_0}$

Dependence of Reaction Rate on Temperature

Reactions almost always occur faster at higher temperature. Quantified by the <u>Arrhenius Equation</u> for the rate constant

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

    A = frequency factor
    E_a = activation energy
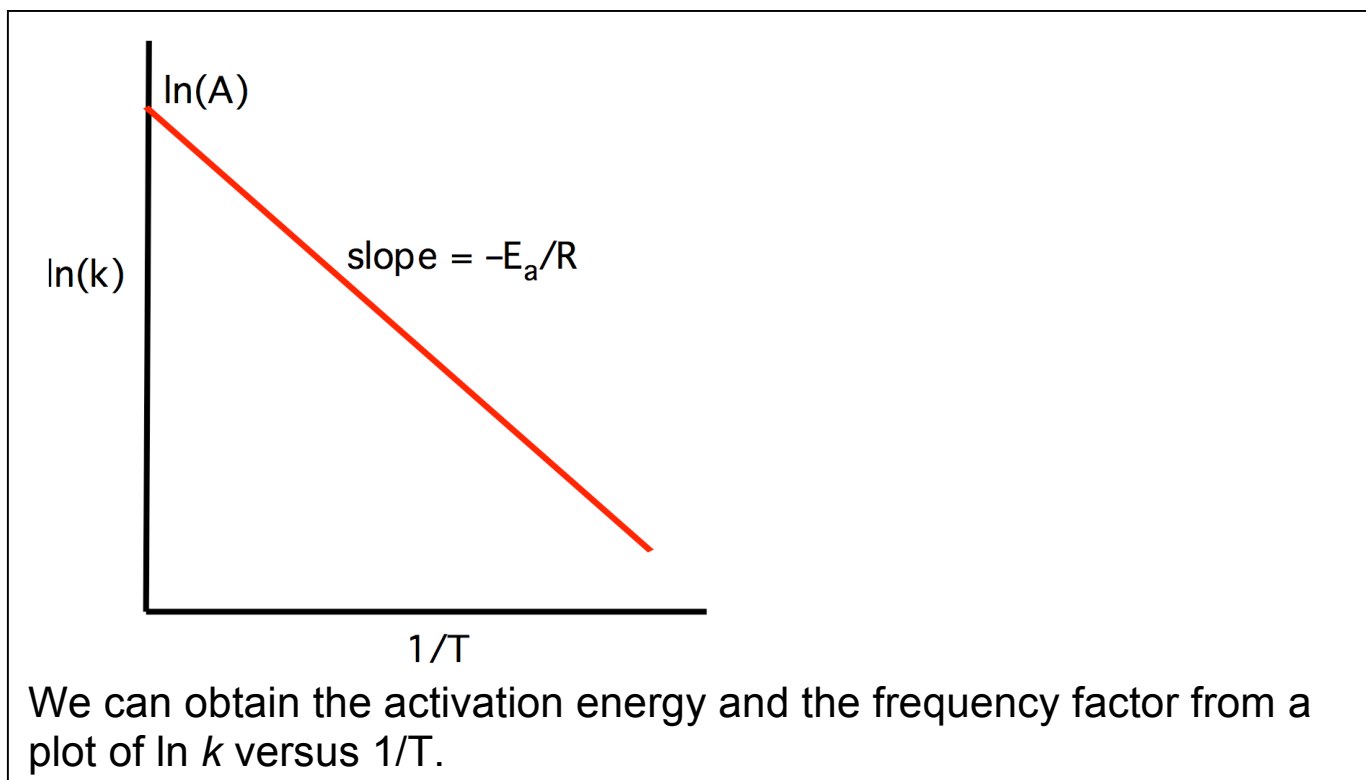 R = gas constant = 8.314 J K^{-1} mol^{-1}
    T = temperature (in K)

Increase E_a : decrease k
Increase T : increase k

Take the logarithm of the Arrhenius Equation:

$$\ln k = \ln A - \frac{E_a}{RT} \qquad (\text{used } \ln xy = \ln x + \ln y)$$

We can obtain the activation energy and the frequency factor from a plot of ln k versus 1/T.

Now, consider two different temperatures:

$$\ln k_1 = \ln A - \frac{E_a}{RT_1} \quad (1) \qquad \text{and} \qquad \ln k_2 = \ln A - \frac{E_a}{RT_2} \quad (2)$$

Subtract (1) – (2) to obtain

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

e.g., Determine E_a, and also *k* at 655 K, from the data:

T (K)	k (s^{-1})
625	1.1 x 10^{-4}
635	1.5 x 10^{-4}
645	2.0 x 10^{-4}

Solution:

From the first two data points,

$$\ln \frac{1.1}{1.5} = \frac{E_a}{R}\left(\frac{1}{635\,\text{K}} - \frac{1}{625\,\text{K}}\right) \quad \Rightarrow \quad -0.31 = (E_a/R)(-2.52 \times 10^5 \,\text{K}^{-1})$$

$$E_a = (-0.31)(8.314\,\text{J K}^{-1}\text{mol}^{-1})/(-2.52 \times 10^5 \,\text{K}^{-1}) = 102.3\,\text{kJ/mol}$$

Then, using T = 645 K and T = 655 K, we have

$$\ln \frac{2.0}{k} = \frac{102.3 \times 10^3 \,\text{J mol}^{-1}}{8.314\,\text{J K}^{-1}\text{mol}^{-1}}\left(\frac{1}{655\,\text{K}} - \frac{1}{645\,\text{K}}\right) = -0.291$$

$$\Rightarrow \ln 2.0 \times 10^{-4} - \ln k = -0.291 \quad \Rightarrow \quad \ln k = -8.226$$

$$\Rightarrow \quad k = e^{-8.226} = 2.7 \times 10^{-4}$$

Reaction Mechanisms

- o Most reactions occur in a series of steps
- o The balanced equation does not tell us how the reaction occurs!
- o The series of steps is the reaction mechanism

Consider the reaction $2\ NO(g) + O_2(g) \rightarrow 2\ NO_2(g)$

This reaction cannot occur as written because
1. The simultaneous collision of 3 molecules is unlikely
2. N_2O_2 is detected during the course of the reaction

Possible mechanism:

elementary rxn 1: $NO + NO \rightarrow N_2O_2$ (slow)
elementary rxn 2: $N_2O_2 + O_2 \rightarrow 2\ NO_2$ (fast)

The elementary reactions must add up to give the overall rxn.
Rate determining step: slowest step in the rxn mechanism
(elementary step with the largest activation energy)
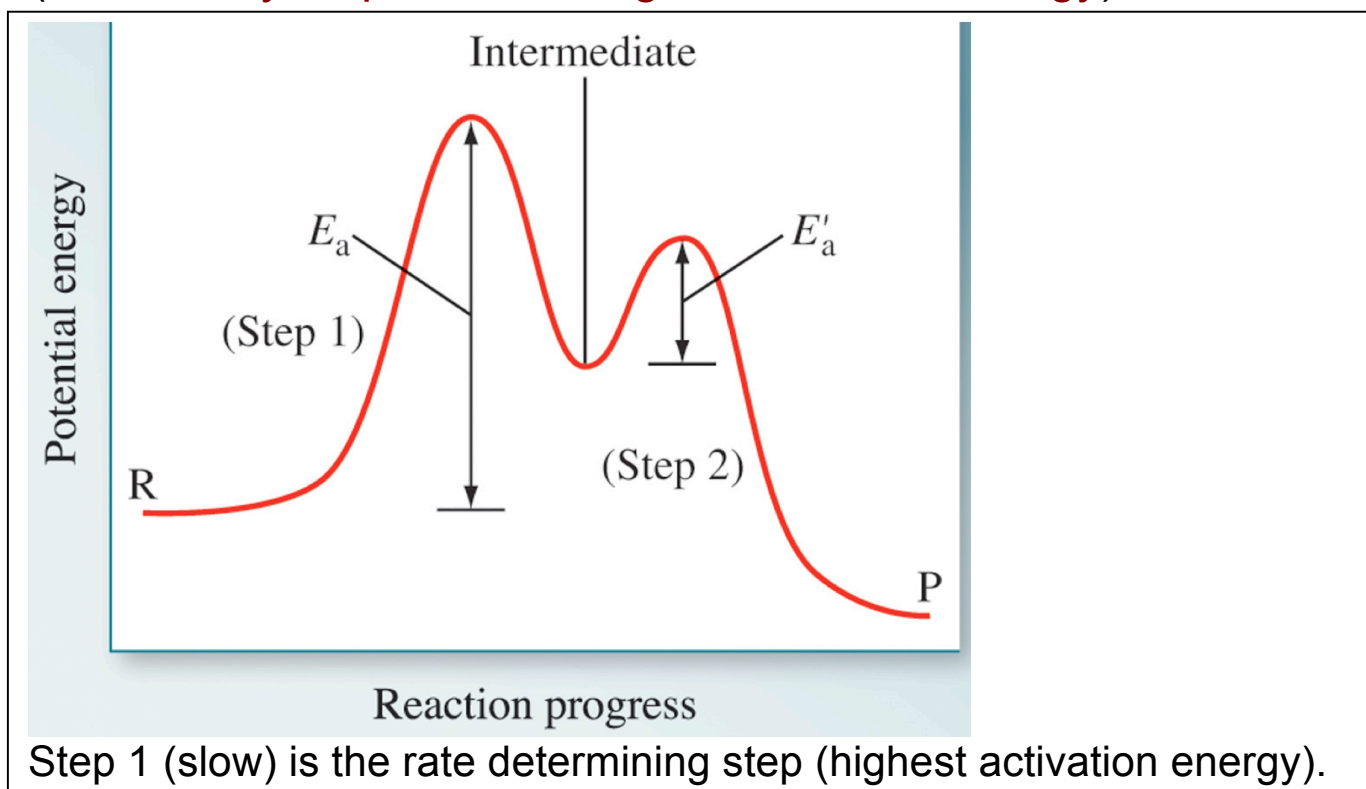
Step 1 (slow) is the rate determining step (highest activation energy).

N_2O_2 is called an *intermediate* because
   1. It appears in the mechanism but not in the balanced Eq.
   2. It is produced in one step and consumed in a later step.

For each elementary reaction, the rate law is given by the stoichiometry coefficients:

elementary rxn 1: $NO + NO \rightarrow N_2O_2$ (slow)
rate$_1$ = k_1[NO]^2

elementary rxn 2: $N_2O_2 + O_2 \rightarrow 2\ NO_2$ (fast)
rate$_2$ = k_2[N$_2$O$_2$][O$_2$]

The rate law of the rate-determining step must be ***equal*** to the overall reaction rate law.

For $2\ NO(g) + O_2(g) \rightarrow 2\ NO_2(g)$ this is: rate = k[NO]^2

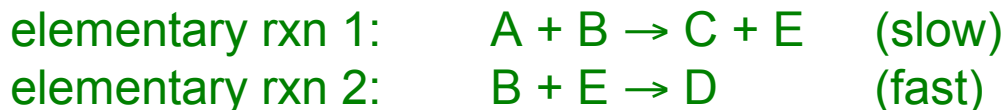For the reaction $H_2 + 2ICl \rightarrow 2HCl + I_2$ the experimentally determined rate law = k[H2][ICl].

What reaction mechanism is consistent with this information?

   elementary rxn 1: $H_2 + ICl \rightarrow HCl + HI$ (slow)
   elementary rxn 2: $HI + ICl \rightarrow HCl + I_2$ (fast)

e.g., Propose a plausible mechanism for the reaction
$$A + 2B \rightarrow C + D \text{ given that the rate law is } k[A][B]$$

Solution:

|		
elementary rxn 1:	$A + B \rightarrow C + E$	(slow)
elementary rxn 2:	$B + E \rightarrow D$	(fast)

Mechanisms with a Fast First Step

Consider the reaction $2NO(g) + Cl_2(g) \rightarrow 2NOCl(g)$ with experimentally determined rate = $k[NO]^2[Cl_2]$.

One possibility is that this reaction *is* an elementary step. But this is unlikely because it would require 3 molecules simultaneously colliding.

A more plausible mechanism is

elementary rxn 1:	$NO + Cl_2 \rightarrow NOCl_2$	(fast)
elementary rxn 2:	$NOCl_2 + NO \rightarrow 2NOCl$	(slow)
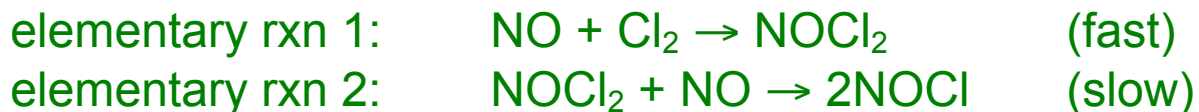
The overall rate law is given by the rate-determining step, which gives rate = $k[NOCl_2][NO]$

But this rate expression contains an *intermediate*, $NOCl_2$. We need an expression that only contains the reactants, or else we can't compare to the experimental rate law.

Since $NOCl_2$ is produced quickly and consumed slowly, it reaches a *steady state* concentration, and the first (fast) step establishes a dynamic equilibrium (forward = backward rate).

We express this as:

$$NO + Cl_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} NOCl_2$$

`
$$NOCl_2 + NO \overset{k_2}{\rightarrow} 2NOCl$$
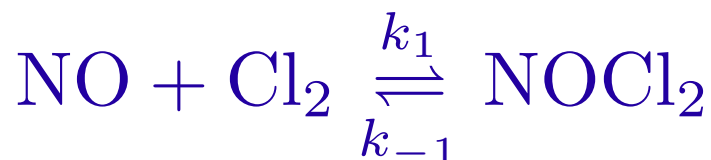
The dynamic equilibrium is
$$k_1[NO][Cl_2] = k_{-1}[NOCl_2]$$
which lets us express
$$[NOCl_2] = \frac{k_1}{k_{-1}}[NO][Cl_2]$$

The rate law is then:
$$\text{rate} = k_2[NOCl_2][NO] = \frac{k_2 k_1}{k_{-1}}[NO]^2[Cl_2]$$

e.g., The reaction $H_2 + I_2 \rightarrow 2HI$ proceeds via a 2-step mechanism in which the rate law for the rate-determining step = $k[H_2][I]^2$. Write the mechanism and rewrite the rate law using only reactant concentrations.

Solution:

$$\text{elementary rxn 1}: \quad I_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2I \quad (\text{fast})$$

$$\text{elementary rxn 2}: \quad H_2 + 2I \overset{k_2}{\rightleftharpoons} 2HI \quad (\text{slow})$$

The dynamic equilibrium is $k_1[I_2] = k_{-1}[I]^2$

so that $[I]^2 = \dfrac{k_1}{k_{-1}}[I_2] \quad \Rightarrow \quad \text{rate} = \dfrac{k_2 k_1}{k_{-1}}[H_2][I_2]$

Catalyst:

In the presence of iodide ions (I⁻), the decomposition of hydrogen peroxide *speeds up*.

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

Experimental rate law = $k[H_2O_2][I^-]$

elementary rxn 1: $H_2O_2 + I^- \rightarrow H_2O + IO^-$ (slow)
elementary rxn 2: $H_2O_2 + IO^- \rightarrow H_2O + O_2 + I^-$ (fast)
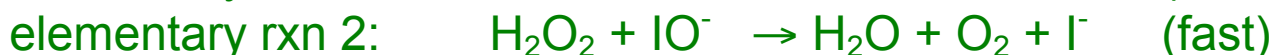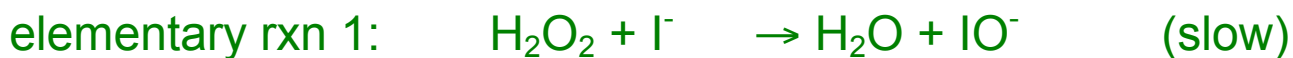
Recall that IO⁻ is called an *intermediate* because
   1. It appears in the mechanism but not in the balanced Eq.
   2. It is produced in one step and consumed in a later step.

What about the iodide ion?
   1. It, also, does not appear in the balanced Eq.
   2. It is consumed in one step and produced in a later step.

It is present at the start of the rxn, and it is present at the end. It is called a catalyst. Its function is to *speed up* the reaction.

A catalyst lowers the activation energy for a chemical reaction.
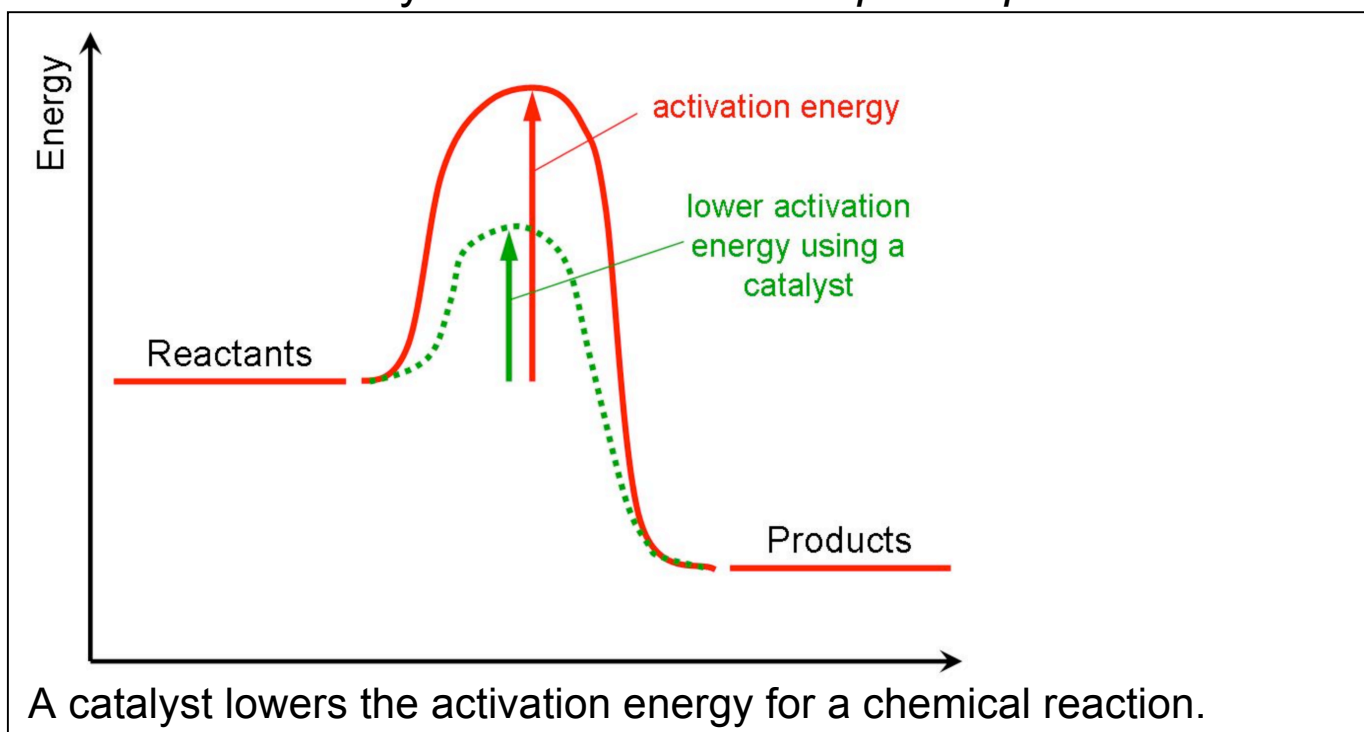
Types of Catalysts

Heterogeneous catalysts: The reactants and catalyst are in different phases. The catalyst is often a solid (with a high surface area).
These are extremely important in industrial chemistry.

Homogeneous catalysts: The reactants and catalyst are in the same phase.

Enzyme catalysts: biological catalysts (in living cells)

A biological catalyst (E = enzyme) lowers the activation energy for a chemical reaction.