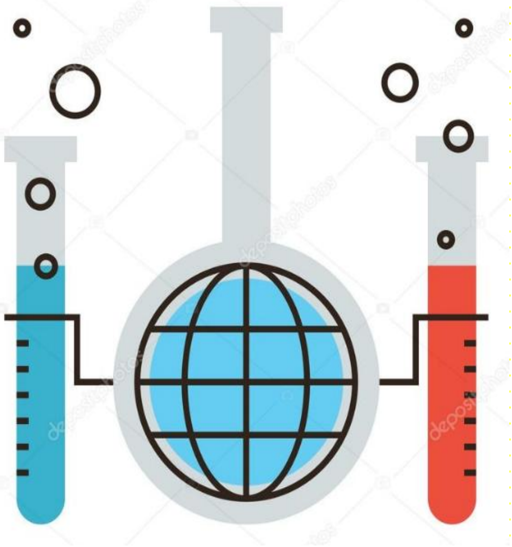
Chapter (5)



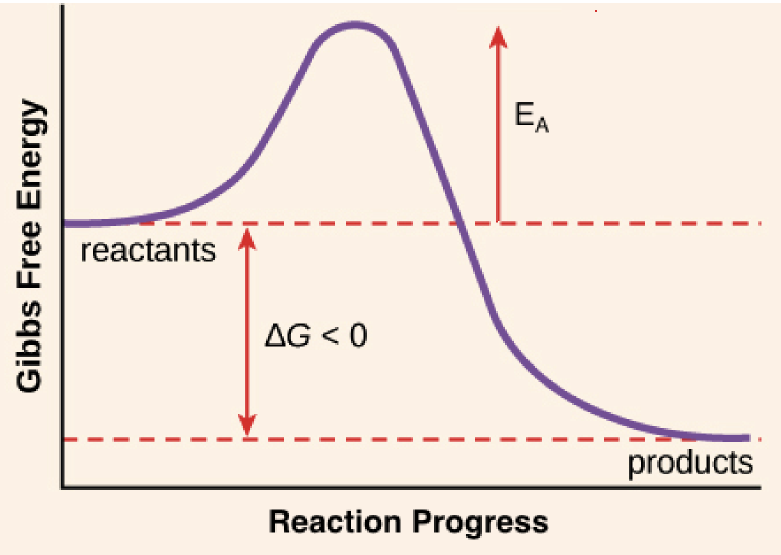
Kinetics of Elementary Chemical Reactions

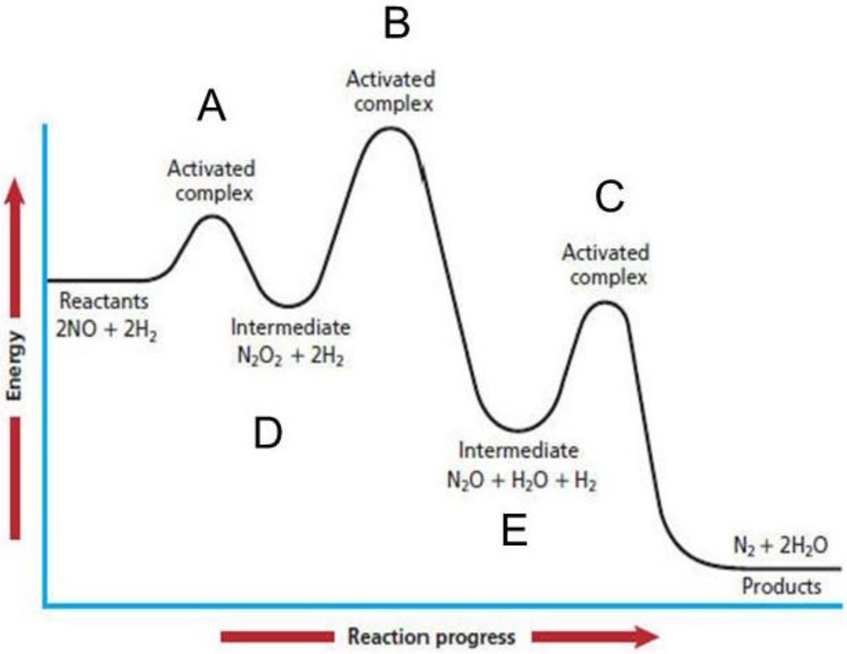
Feb., 3rd , 2018

Reaction Thermodynamics vs. Kinetics

- **Thermodynamics**
  - Will reaction occur or not.
  - Direction of change (forward or backward)
  - State of equilibrium.
  - Key parameter: **Energy**

- **Kinetics**
  - Rate (speed) of change
  - Reaction mechanism
  - Key variable: **Time**





Reaction Thermodynamics vs. Kinetics

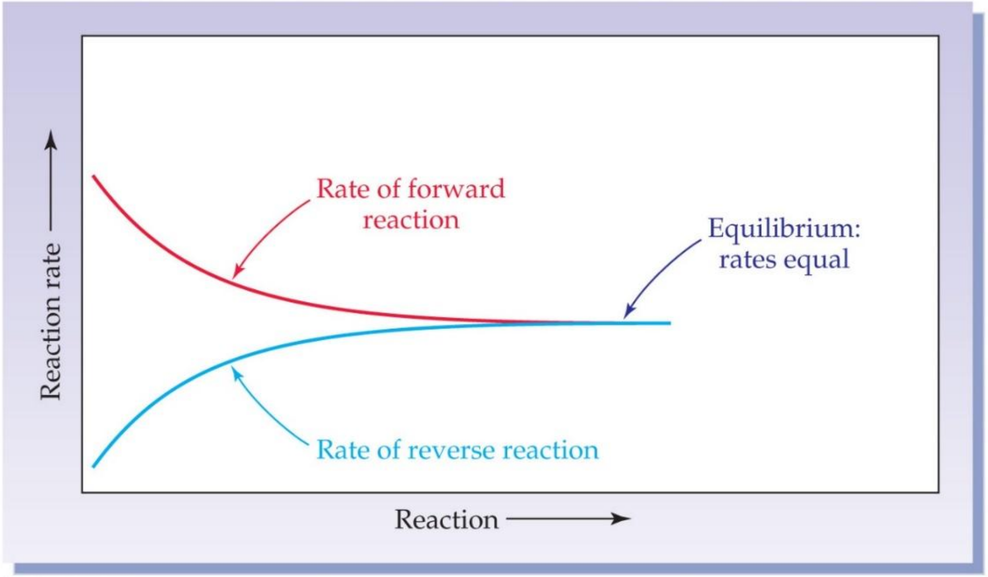
Some reactions that are thermodynamically feasible are kinetically so slow as to be imperceptible

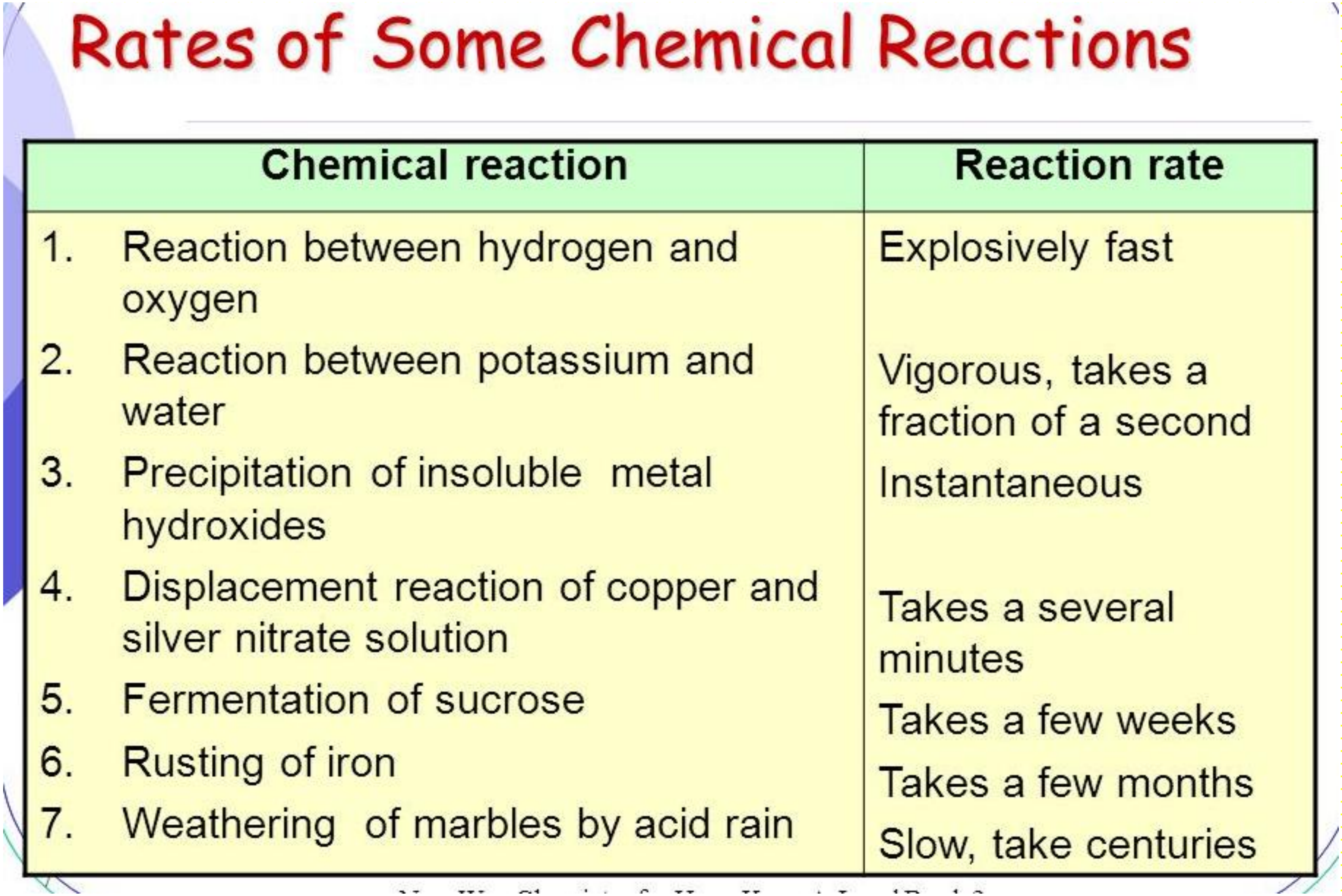
$$C_{diamond} + O_{2(g)} \rightarrow CO_{2(g)} \quad \Delta G^{o}_{298} = -396kJ$$

VERY SLOW

$$H^{+}_{(aq)} + OH^{-}_{(aq)} \rightarrow H_2O_{(l)} \quad \Delta G^{o}_{298} = -79\,kJ$$

INSTANTANEOUS





Rates of Some Chemical Reactions

Chemical reaction	Reaction rate
1. Reaction between hydrogen and oxygen	Explosively fast
2. Reaction between potassium and water	Vigorous, takes a fraction of a second
3. Precipitation of insoluble metal hydroxides	Instantaneous
4. Displacement reaction of copper and silver nitrate solution	Takes a several minutes
5. Fermentation of sucrose	Takes a few weeks
6. Rusting of iron	Takes a few months
7. Weathering of marbles by acid rain	Slow, take centuries

Chemical kinetics

- Study of **mechanism and speed (rate)** of reactions
- Important in determination of
  1. Residence time
  2. Reactor volume (design)
  3. Rate limiting step if more than one
- Reaction kinetics is based on stoichiometry and lab experiments

Chemical kinetics

Mechanism: A series of elementary steps that make up a complex reaction

$$A + B + 2\,C \rightarrow D + E$$

Possible mechanism:

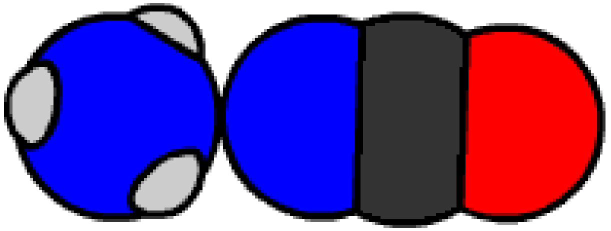
$$A + B \rightarrow F$$

$$F + C \rightarrow G + D$$

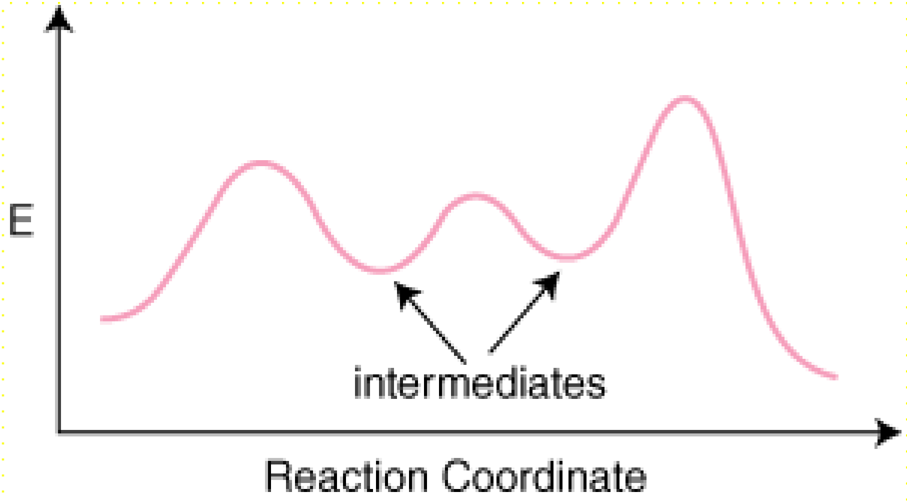
$$G + C \rightarrow E$$

F and G: reaction intermediates

$[NH_4^+][NCO^-]$



Energy curve for multi-step reaction



Reaction Mechanism

- Chemical equation: Summary
- Mechanism: Series of elementary steps
- Elementary Steps: Reactions with rate laws from molecularity
- Molecularity: Number of species that must collide to produce reaction

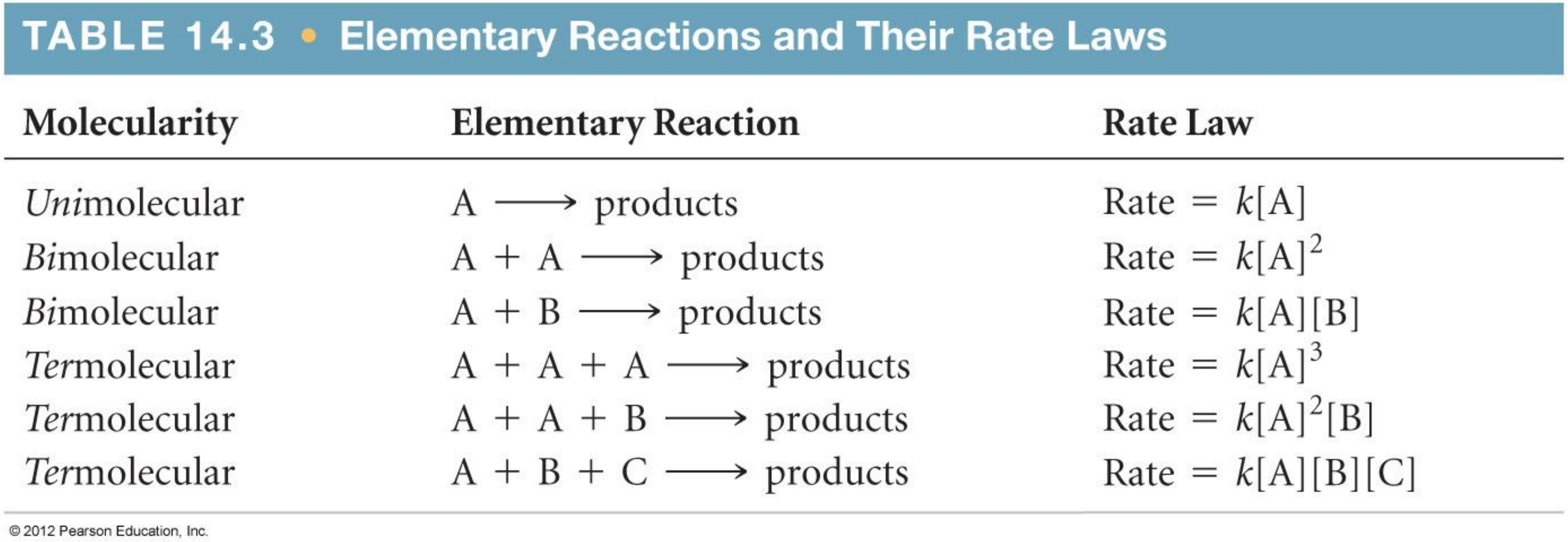


TABLE 14.3 • Elementary Reactions and Their Rate Laws

Molecularity	Elementary Reaction	Rate Law
*Uni*molecular	$A \longrightarrow \text{products}$	$\text{Rate} = k[A]$
*Bi*molecular	$A + A \longrightarrow \text{products}$	$\text{Rate} = k[A]^2$
*Bi*molecular	$A + B \longrightarrow \text{products}$	$\text{Rate} = k[A][B]$
*Ter*molecular	$A + A + A \longrightarrow \text{products}$	$\text{Rate} = k[A]^3$
*Ter*molecular	$A + A + B \longrightarrow \text{products}$	$\text{Rate} = k[A]^2[B]$
*Ter*molecular	$A + B + C \longrightarrow \text{products}$	$\text{Rate} = k[A][B][C]$

Reaction Rates

Reaction rate is the change in the concentration of a reactant or a product with time (M/s).

$$\mathbf{A} \longrightarrow \mathbf{B}$$

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

$\Delta[A]$ = change in concentration of A over time period Δt

Because [A] decreases with time, $\Delta[A]$ is negative.

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

$\Delta[B]$ = change in concentration of B over time period Δt

UNITS: mol/L x 1/s = $\text{mol.L}^{-1}.\text{s}^{-1}$ or M.s^{-1}

Rate of Reaction

Thus rate of reaction can be expressed in terms of the rate of consumption or disappearance of the reactant or the rate of formation of the product.

$$N_2 + O_2 \longrightarrow 2NO$$

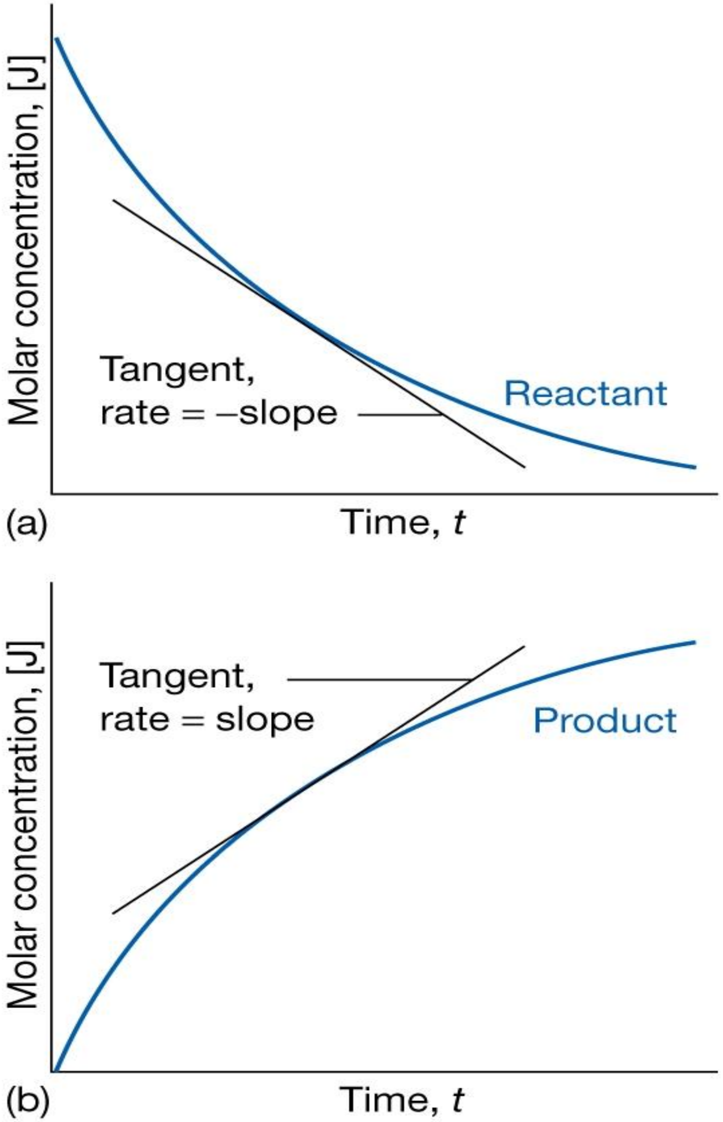
$$\text{Rate in terms of reactants} = -\frac{d[N_2]}{dt} = -\frac{d[O_2]}{dt}$$

$$\text{Rate in terms of product} = \frac{d[NO]}{dt}$$

Considering the stoichiometry of the reaction the rate of the reaction can be expressed as

$$\boxed{-\frac{d[N_2]}{dt} = -\frac{d[O_2]}{dt} = \frac{1}{2}\frac{d[NO]}{dt}}$$

Change of reaction rate with time



Concentration and rate

$A + B \rightarrow$ products

In general it is found that:

$$r \propto [A]^m[B]^n$$

The values of the **exponents, m and n**, must be determined empirically (by experiment).

We can **replace ∝ by =** if we introduce a **rate constant, k.**

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

This expression is the *rate law*

(Experimental rxn rate)

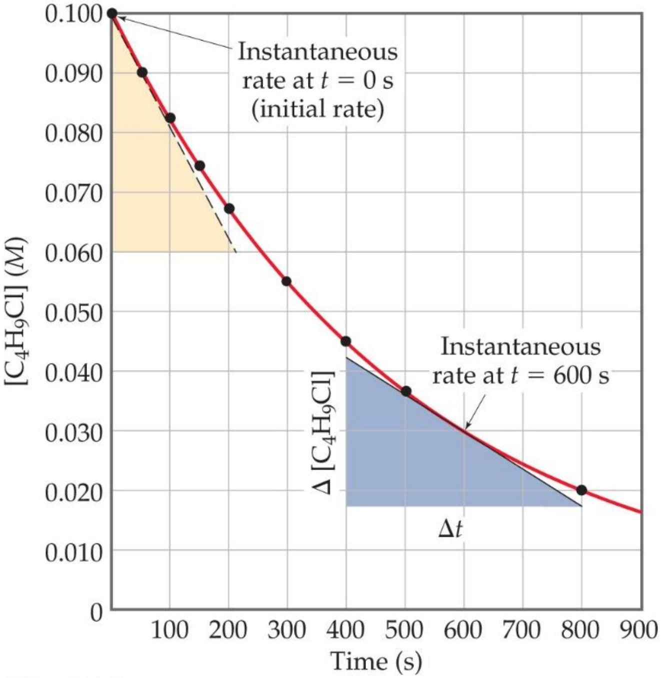
Change of reaction rate with time

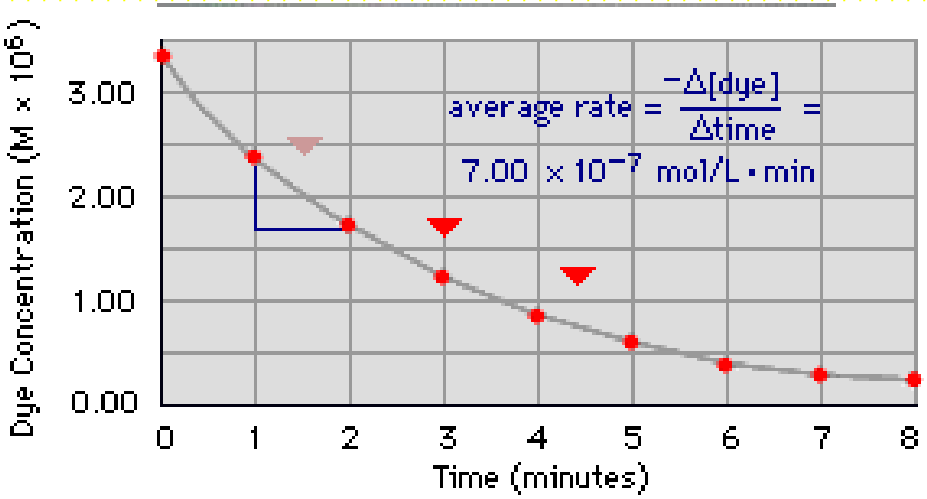
$$\text{rate} = \frac{\Delta\ \text{concentration}}{\Delta\ \text{time}}$$

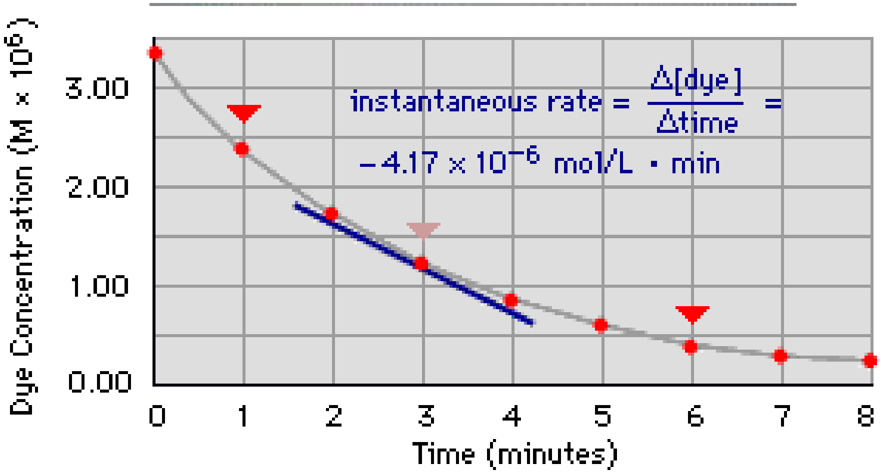
Types of measured rates:

- Rate over time:
- Instantaneous rate:
- Initial rate:

$C_4H_9Cl(aq) + H_2O(l) \longrightarrow C_4H_9OH(aq) + HCl(aq)$







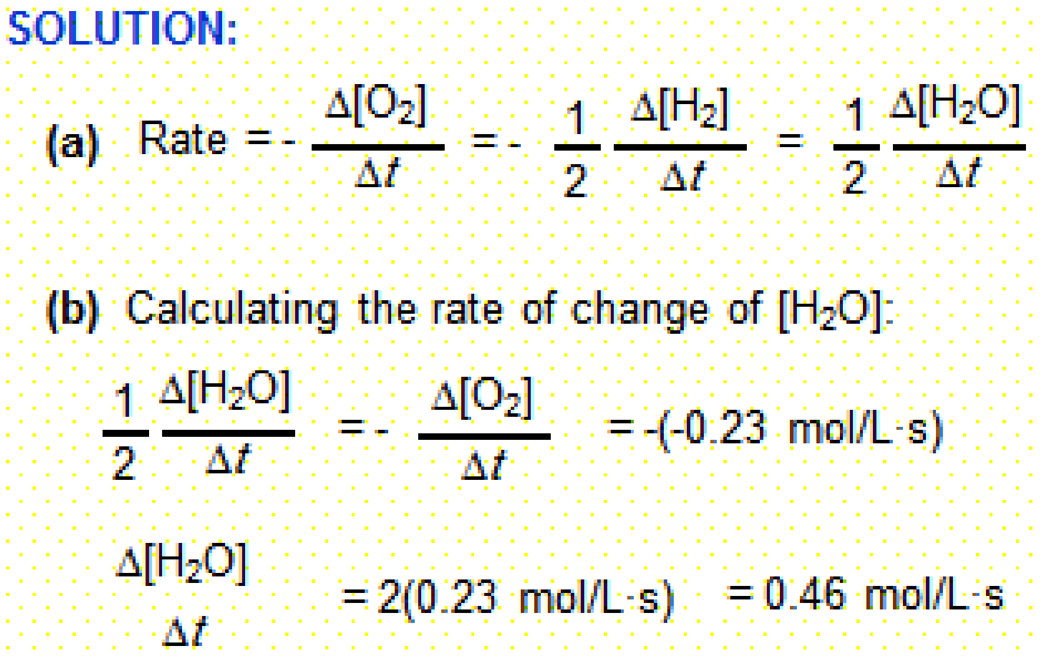
Example: Rate in Terms of Changes in Concentration with Time

Hydrogen gas has a nonpolluting combustion product (water vapor). It is used as a fuel abord the space shuttle and in earthbound cars with prototype engines:

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(g)$$

(a) Express the rate in terms of changes in $[H_2]$, $[O_2]$, and $[H_2O]$ with time.

(b) When $[O_2]$ is decreasing at 0.23 mol/L·s, at what rate is $[H_2O]$ increasing?



SOLUTION:

(a) $$\text{Rate} = -\frac{\Delta[O_2]}{\Delta t} = -\frac{1}{2}\frac{\Delta[H_2]}{\Delta t} = \frac{1}{2}\frac{\Delta[H_2O]}{\Delta t}$$

(b) Calculating the rate of change of $[H_2O]$:

$$\frac{1}{2}\frac{\Delta[H_2O]}{\Delta t} = -\frac{\Delta[O_2]}{\Delta t} = -(-0.23\ \text{mol/L·s})$$

$$\frac{\Delta[H_2O]}{\Delta t} = 2(0.23\ \text{mol/L·s}) = 0.46\ \text{mol/L·s}$$

Reaction Rates and Stoichiometry

$$a\,\mathrm{A} + b\,\mathrm{B} \longrightarrow c\,\mathrm{C} + d\,\mathrm{D}$$

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

Above is the relationship between overall reaction rate and rates of consumption of reactants and rates of formation of products.

FOR EXAMPLE

$$3O_{2(g)} \rightarrow 2O_{3(g)}$$

$$rate = -\frac{1}{3}\frac{O_2}{\Delta t} = \frac{1}{2}\frac{O_3}{\Delta t}$$

Experimental techniques

- Monitoring concentrations:

  Depends on the species involved and the rapidity with which their concentrations changes.

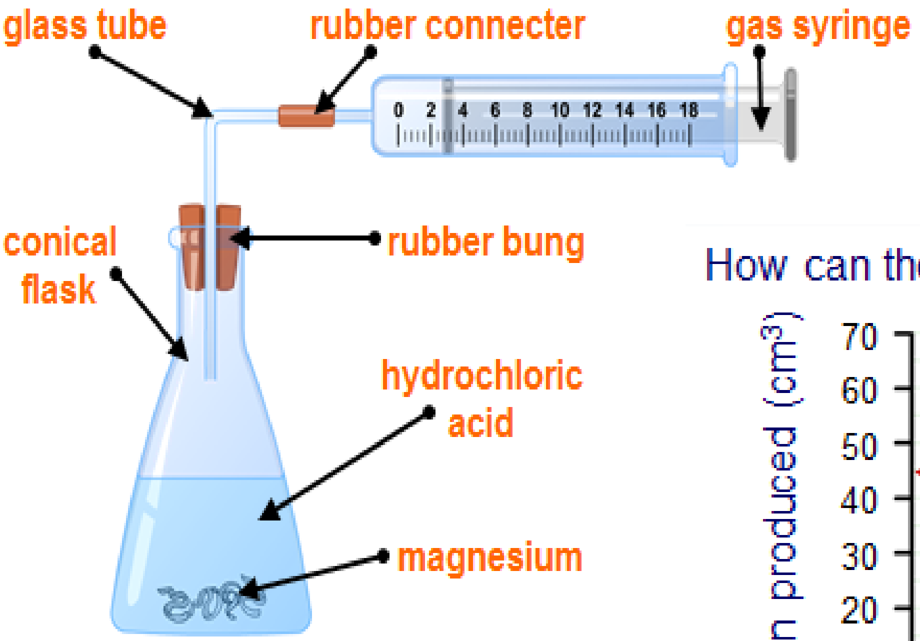
  1. spectrophotometry.
  2. electrical conductivity
  3. pH of the solution
  4. redox potential

- Determining the compositions of a solution:

  1. mass spectrometry
  2. gas chromatography
  3. emission spectroscopy
  4. nuclear magnetic resonance
  5. electron spin resonance

Measuring Reaction Rate

What equipment is needed to investigate the rate of hydrogen production?



glass tube

rubber connecter

gas syringe

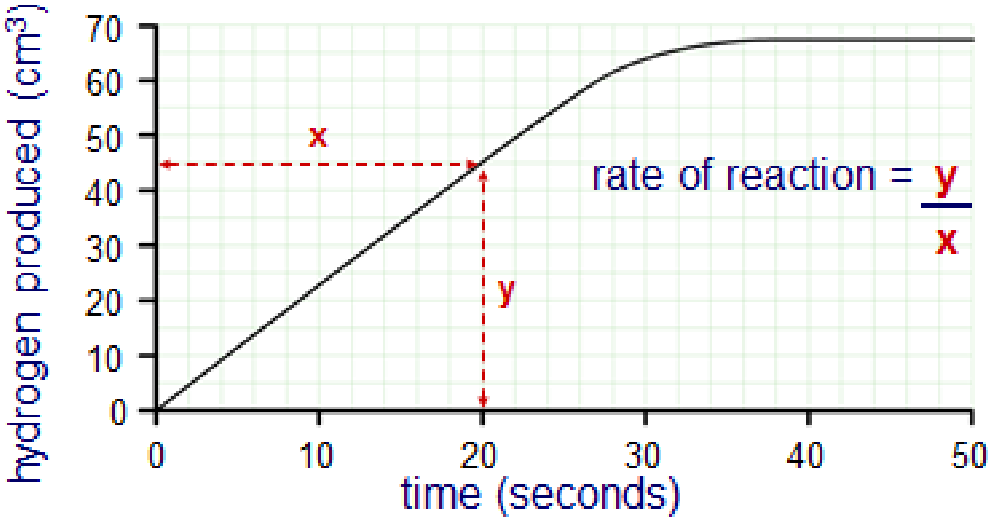
conical flask

rubber bung

hydrochloric acid

magnesium

How can the rate of reaction be calculated from a graph?



rate of reaction = $\frac{y}{x}$

The gradient of the graph is equal to the initial rate of reaction at that time

rate of reaction = $\frac{45\,\text{cm}^3}{20\,\text{s}}$ rate of reaction = **2.25 cm^3/s**

Measuring Reaction Rate

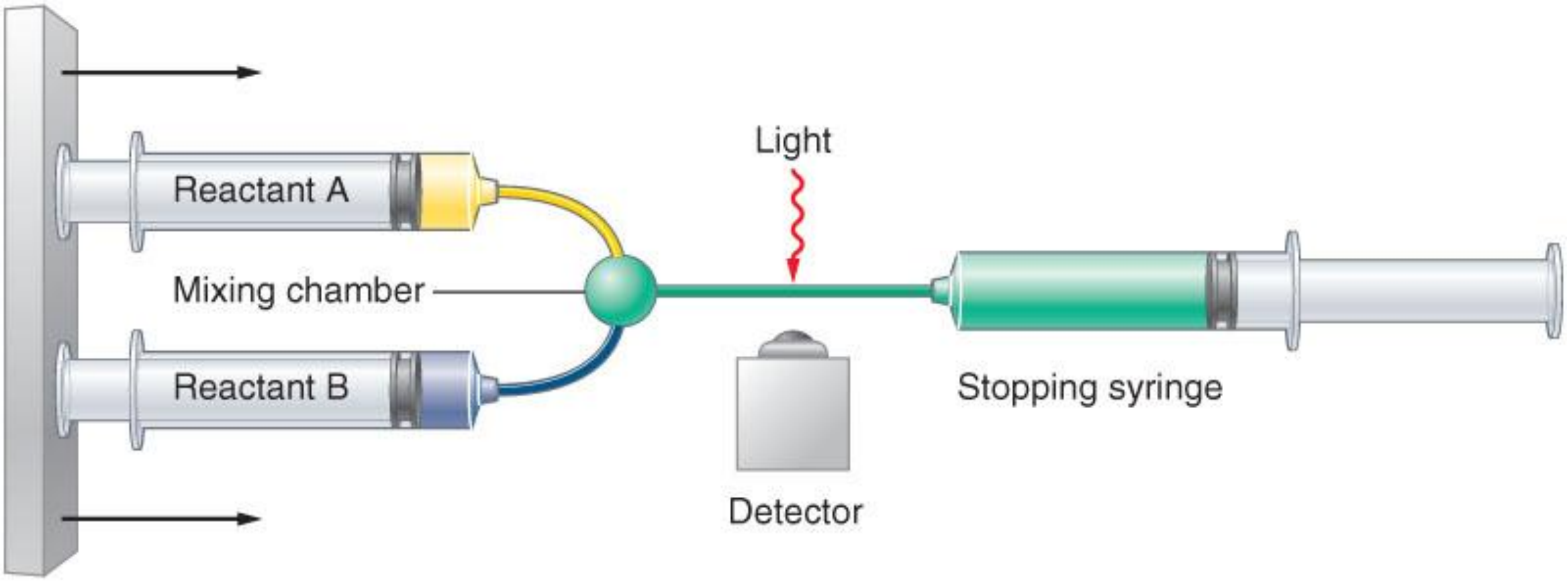


Figure Schematic of a **stopped-flow experiment**.

Two reactants are rapidly introduced into the mixing chamber by syringes. After mixing chamber, the reaction kinetics are monitored by observing the change in sample concentration versus time, in this example by measuring the absorption of light as a function of time after mixing.

Reaction Rates

How fast does a reaction process occur? Reaction rates are controlled by:

1. **Nature of reactants:** substances are different in their mobility in the reaction mixture as well as their reactivity.
    1. Ions in solution react quickly.
    2. Covalently bonded molecules react slowly. It takes time to break all those bonds!
    3. Two gas phase reactants tend to react more quickly than 2 liquids or 2 solids.
2. **Ability of reactants to meet & collide:** In order to react, molecules must come in contact with each other. The more homogeneous the mixture of reactants, the faster the molecules can react. The rate of reaction is usually determined the frequency of successful collisions.
3. **Concentration of reactants:** Increase in concentration means more particles (molecules or ions) per unit volume, thus so more collisions in a given amount of time. For gases, pressure has the same effect as concentration.

Reaction Rates

How fast does a reaction process occur? Reaction rates are controlled by:

3. **Temperature:**
    - At higher temperatures, reactant molecules have more kinetic energy, move faster and collide more often and with greater energy.
    - Increases the frequency of collisions and increases the percentage of collisions that lead to reaction.
    - Rule of thumb: Increasing the temperature 10oC doubles the reaction rate.
4. **Presence of a catalyst**. Catalysts speed up reactions by changing the mechanism of reaction. They are not consumed during the course of the reaction.
5. **Surface area of solids** (For heterogeneous reactions involving reactants or catalysts).
    - Higher surface area, more particles exposed for reaction.
    - Higher surface area means smaller particle size

The Rate law

1. The **rate law** expresses the relationship of the rate of a reaction to the rate constant and the concentrations of the reactants raised to some powers.
2. Rate laws are always determined experimentally.
3. Reaction order is always defined in terms of reactant (not product) concentrations.
4. The order of a reactant is not related to the stoichiometric coefficient of the reactant in the balanced chemical equation.

- For any general reaction occurring at a fixed temperature

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

$$\boxed{\text{Rate} = k[A]^m[B]^n}$$

The Rate law

$$\boxed{\text{Rate} = k\,[A]^m[B]^n}$$

- The term **k** is the rate constant, which is specific for a given reaction at a given temperature. The exponents **m** and **n** are reaction orders and are determined by experiment. The values of m and n are not necessarily related in any way to the coefficients **a** and **b.**

For the reaction: **$2NO(g) + 2H_2(g) \rightarrow N_2(g) + 2H_2O(g)$**

The rate law is rate: **$r = k\,[NO]^2[H_2]$**

- The reaction is second order with respect to NO, first order with respect to H2 and third order overall. Note that the reaction is first order with respect to H2 even though the coefficient for H2 in the balanced equation is 2. Reaction orders must be determined from experimental data and cannot be deduced from the balanced equation.

Example: Determining Reaction Orders from Rate Laws

For each of the following reactions, use the give rate law to determine the reaction order with respect to each reactant and the overall order.

(a) $2NO(g) + O_2(g) \rightarrow 2NO_2(g)$; rate = $k[NO]^2[O_2]$
(b) $CH_3CHO(g) \rightarrow CH_4(g) + CO(g)$; rate = $k[CH_3CHO]^{3/2}$
(c) $H_2O_2(aq) + 3I^-(aq) + 2H^+(aq) \rightarrow I_3^-(aq) + 2H_2O(l)$; rate = $k[H_2O_2][I^-]$

PLAN: We inspect the exponents in the rate law, *not* the coefficients of the balanced equation, to find the individual orders. We add the individual orders to get the overall reaction order.

SOLUTION:

(a) The exponent of [NO] is 2 and the exponent of $[O_2]$ is 1, so the reaction is **second order with respect to NO, first order with respect to O_2** and **third order overall**.

(b) The reaction is $\mathbf{\frac{3}{2}}$ **order in CH_3CHO** and $\mathbf{\frac{3}{2}}$ **order overall.**

(c) The reaction is first order in H2O2, first order in I-, and second order overall. The reactant H+ does not appear in the rate law, so the reaction is zero order with respect to H+.

Example Rate Laws:

$$CO + Cl_2 \rightarrow COCl_2$$

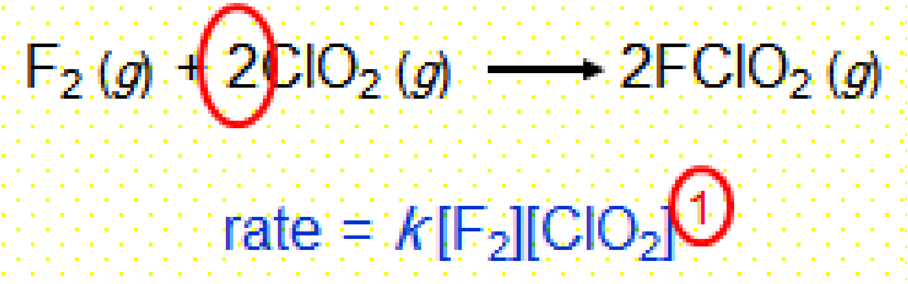
- Rate = k $[CO][Cl_2]^{1/2}$
  - Order = 1.5 or one-and-a-half order

$$H_2 + I_2 \rightarrow 2HI$$

- Rate = k $[H_2][I_2]$
  - Order = 2 or second order

$$H_2 + Br_2 \rightarrow 2HBr$$

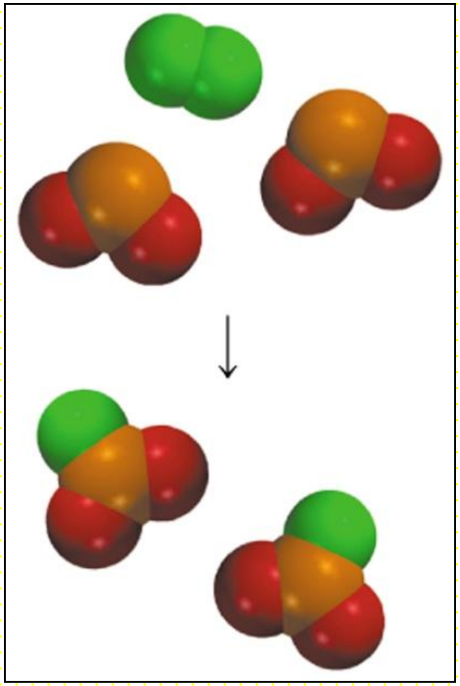
- Rate = k $[H_2][Br_2]$ / (1 + k’ {$[HBr]/[Br_2]$})
  - Order = undefined or none



$$F_2\,(g) + \textcircled{2}ClO_2\,(g) \longrightarrow 2FClO_2\,(g)$$

- Rate law:

$$\text{rate} = k[F_2][ClO_2]^{\textcircled{1}}$$



Determining the Rate Law

- Integration /Graphical
    - Trial & error approach
    - Not suitable for multi-reactant systems
    - Most accurate
- Initial rates
    - Best for multi-reactant reactions
    - Lower accuracy
- Isolation
    - Composite technique
    - Uses integration or initial rates methods

1) Integration /graphical method

First Order Reaction

$$\mathrm{A} \xrightarrow{k} P$$

$$R = k[\mathrm{A}]; \quad R = -\frac{d[\mathrm{A}]}{dt}$$

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

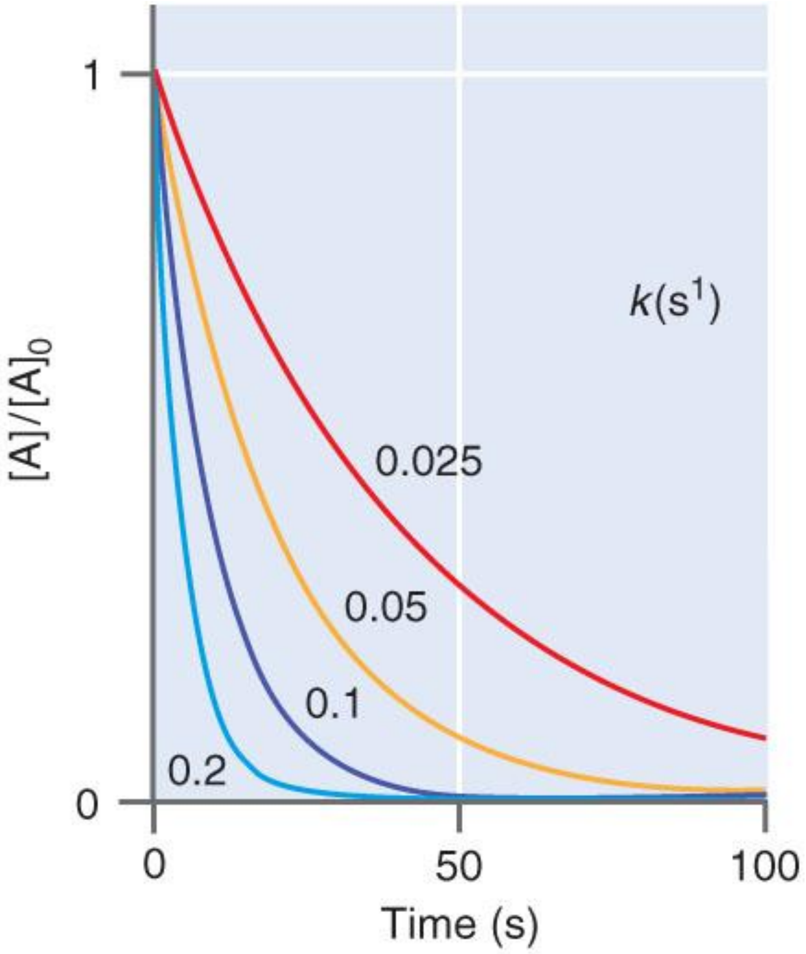
$$\ln\left(\frac{[\mathrm{A}]}{[\mathrm{A}]_0}\right) = -kt; \quad [\mathrm{A}] = [\mathrm{A}]_0 e^{-kt}$$

$$[\mathrm{P}] = [\mathrm{A}]_0 - [\mathrm{A}] = [\mathrm{A}]_0\left(1 - e^{-kt}\right)$$

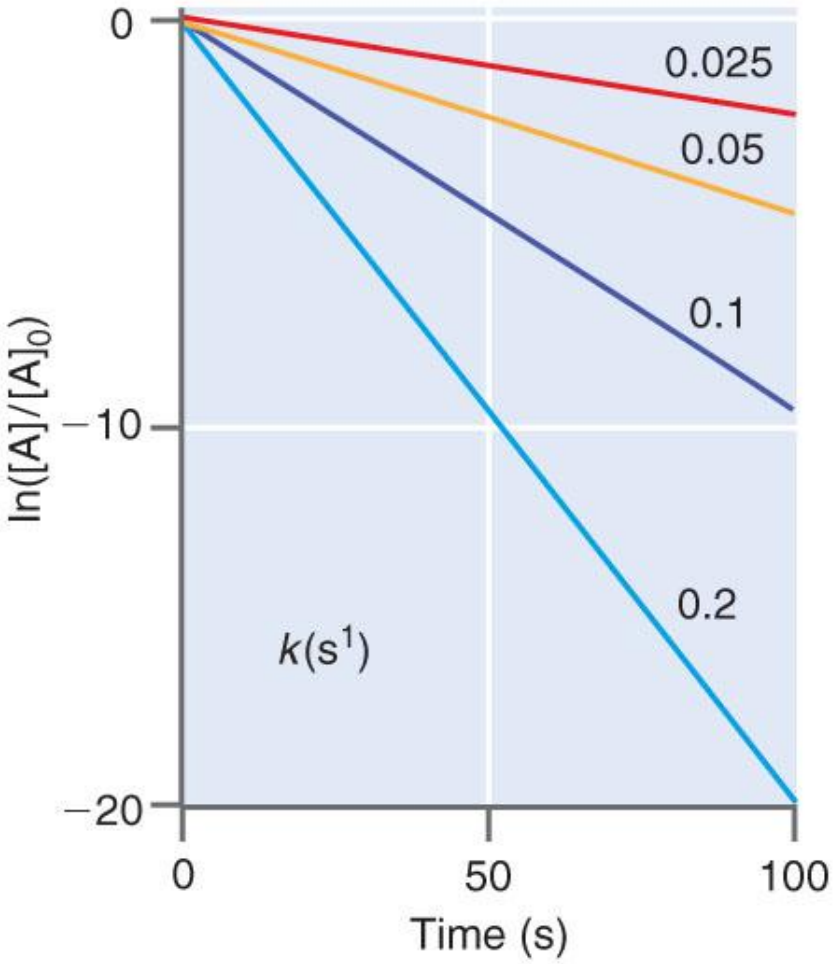
$$\ln[\mathrm{A}] = \ln[\mathrm{A}]_0 - kt$$

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

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



(a)



(b)

Half - life for First - Order Reaction

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

$$k_{1/2} = \frac{\ln 2}{k}$$

- When is a reaction over?

$[A] = [A]_0 \exp\{-k.t\}$

Technically: $[A] = 0$ only after *infinite* time ($t = \infty$)

since: $\exp\{-\infty\} = 0$

Half life: first-order reaction

- The time taken for [A] to drop to half its original value is called the reaction's half-life, $t_{1/2.}$ Setting $[A] = \frac{1}{2}[A]_0$ and $t = t_{1/2}$ in:

$$\text{100\% starting compound} \xrightarrow{t_{1/2}} \text{50\% starting compound} \xrightarrow{t_{1/2}} \text{25\% starting compound}$$

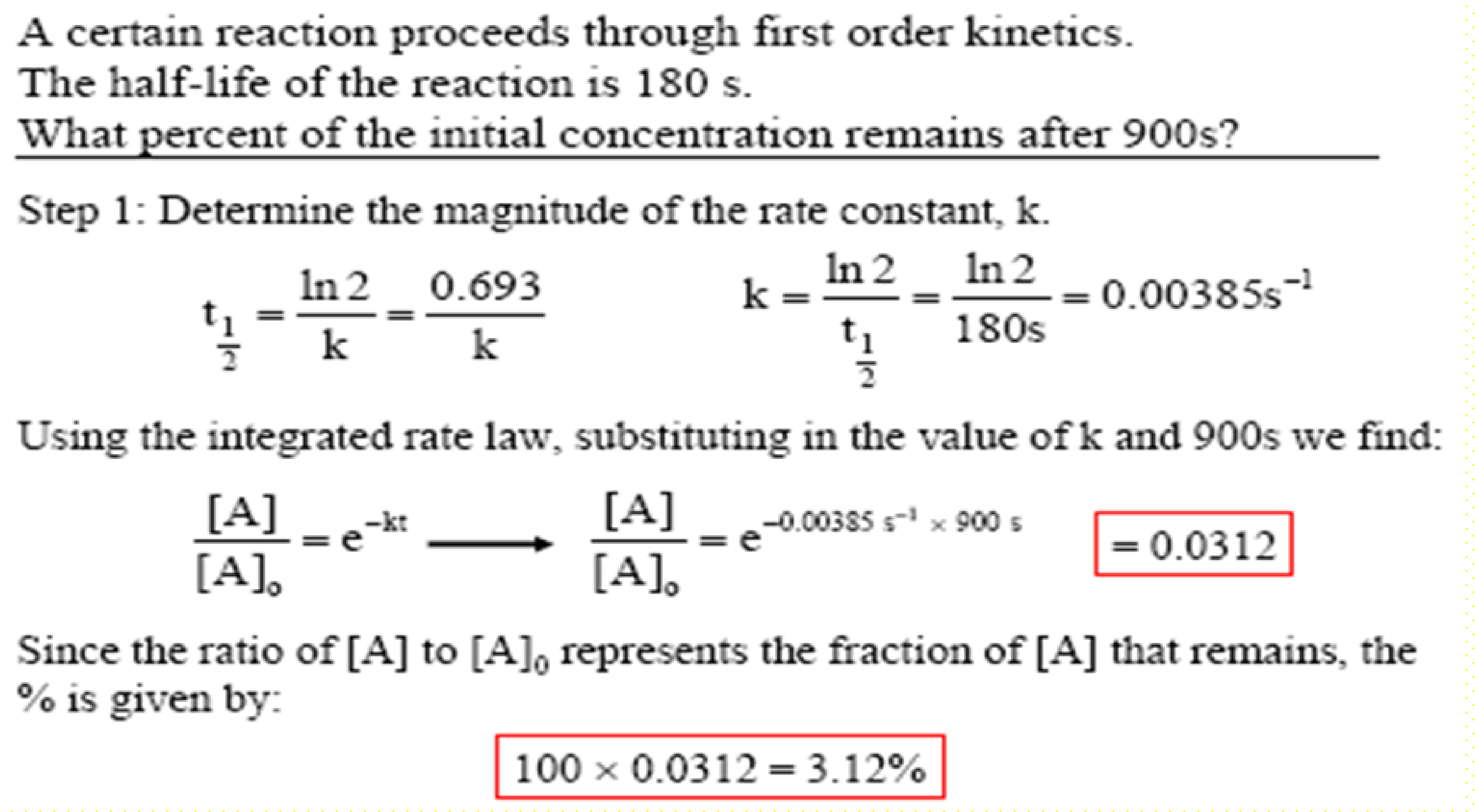
$$\ln\left(\frac{[A]_t}{[A]_0}\right) = -k_A t$$

$$\ln\left(\frac{\frac{1}{2}[A]_0}{[A]_0}\right) = -k_A t_{1/2}$$

$$\ln\left(\frac{1}{2}\right) = -k_A t_{1/2} = -0.693$$

$$\Rightarrow t_{1/2} = \frac{0.693}{k_A} \quad or \quad k_A = \frac{0.693}{t_{1/2}}$$

Half life: first-order reaction



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.

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

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

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

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

$$\boxed{100 \times 0.0312 = 3.12\%}$$

Zero-order reaction

For a zero order rate law: $\mathbf{r = d[A]/dt = - k\,[A]^0 = - k}$

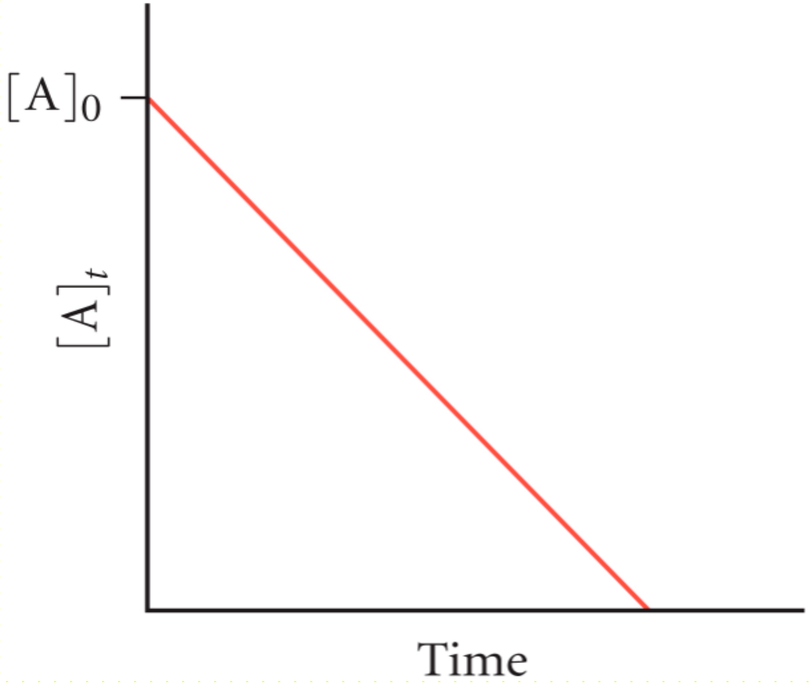
By integration from $[A]_0$ & t=0 to $[A]_t$ @ time, t:

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

where $[A]_t$ = concentration of A at time t

$[A]_0$ = concentration of A at t = 0

k = rate constant (units of concentration/time)



Second-order reaction

2 A → products

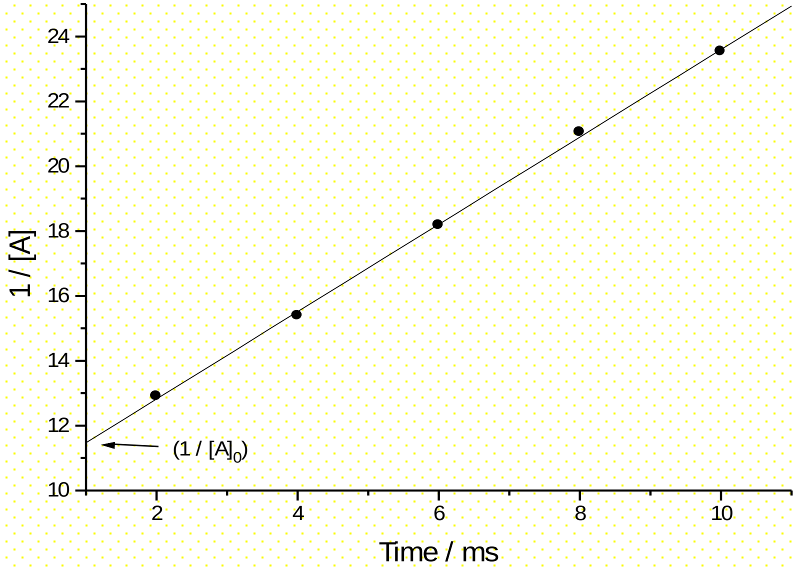
$$r = \frac{d[A]}{dt} = -k_A[A]^2$$

$$\frac{d[A]}{[A]^2} = -k_A dt$$

$$\int_{[A]_0}^{[A]_t} \frac{d[A]}{[A]^2} = -k_A \int_0^t dt$$

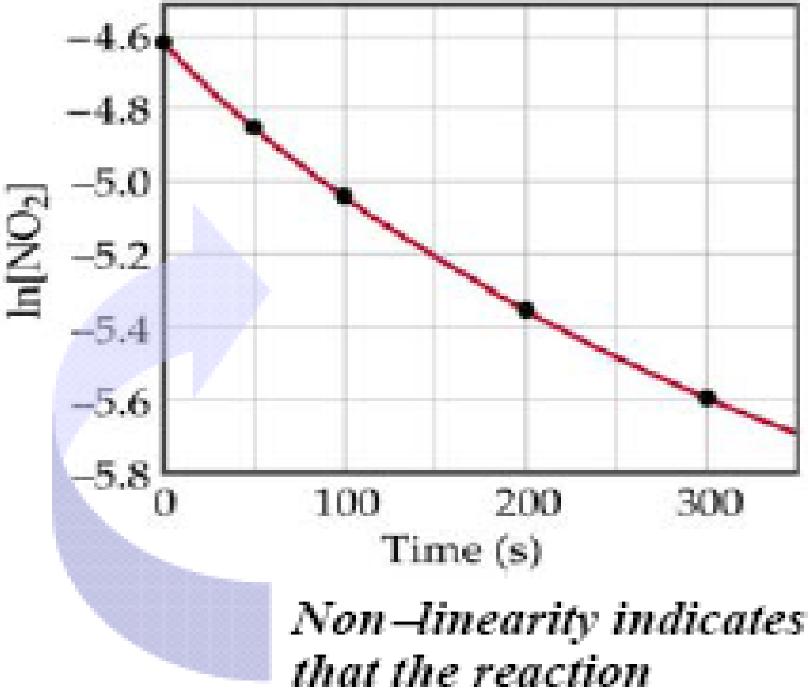
$$\frac{1}{[A]_0} - \frac{1}{[A]_t} = -k_A(t - t_0)$$

$$\frac{1}{[A]_t} - \frac{1}{[A]_0} = k_A t$$

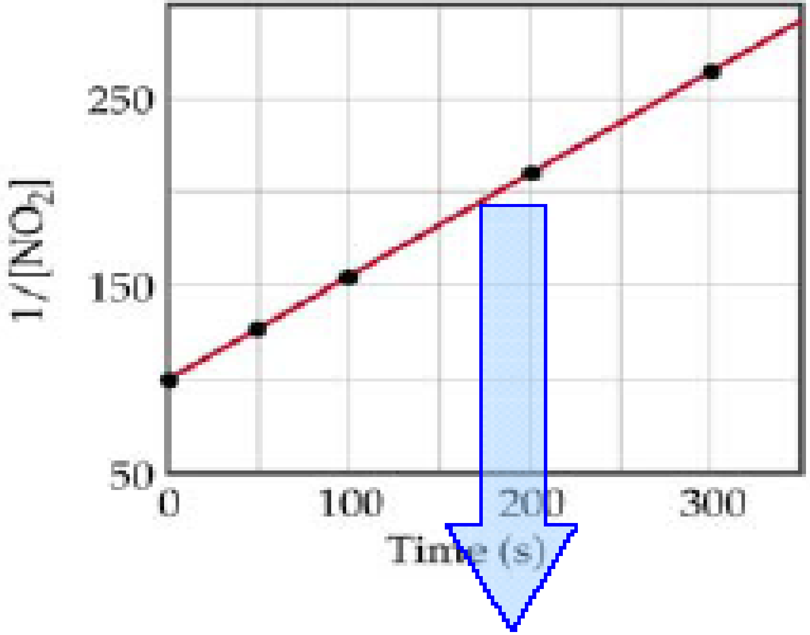


A plot of 1/[A] versus t gives a straight line of slope k_A if $r = k_A[A]^2$

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



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



Slope = k (rate constant)

Half-life: second-order reaction

$$\frac{1}{[A]_t} - \frac{1}{[A]_0} = k_A t$$

$$\frac{2}{[A]_o} - \frac{1}{[A]_0} = k_A t_{1/2}$$

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

Example

$A \rightarrow$ products

- In the decomposition of azomethane, A, at a pressure of 21.8 kPa & a temperature of 576 K the following concentrations were recorded as a function of time, *t*:

Time, *t* /mins	0	30	60	90	120
[A] / mmol dm^{-3}	8.70	6.52	4.89	3.67	2.75

- Show that the reaction is 1st order in azomethane & determine the rate constant at this temperature.

Solution: Rate law – Use Integral method.

$$-\,(d[A]/dt) = k\,[A]^{?} = k\,[A]^{1}$$

Re-arrange & integrate

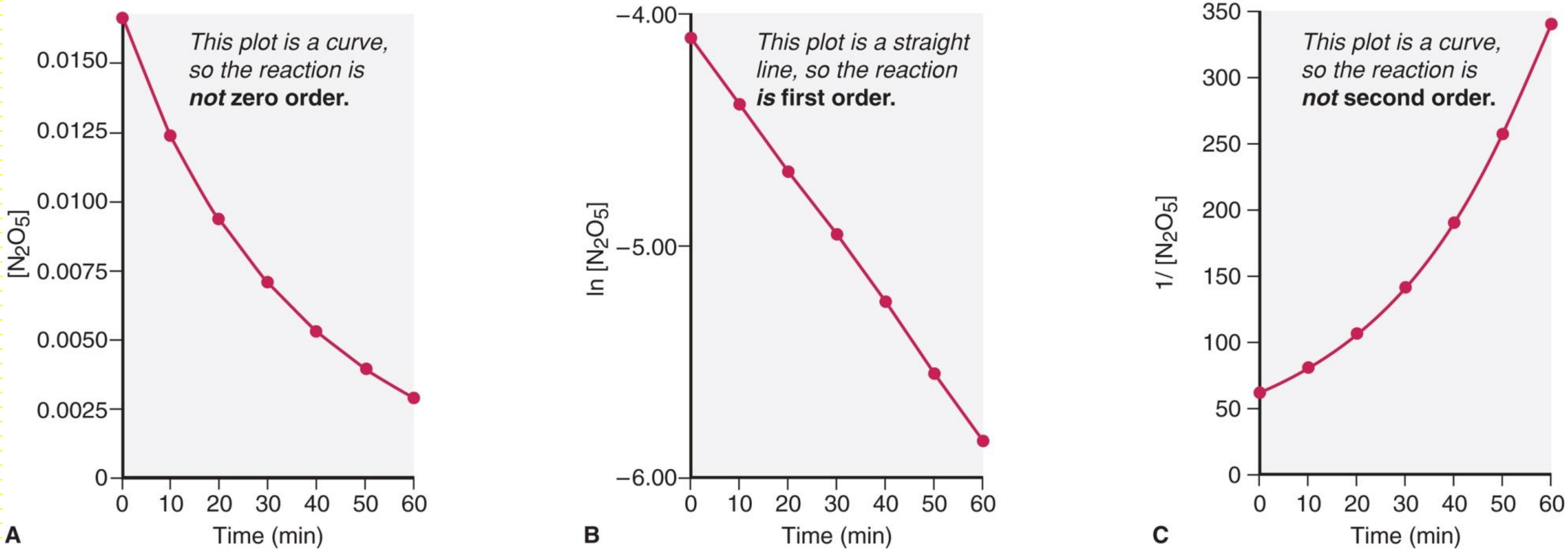
- Test: $\ln[A] = -\,k\,t + \ln[A]_0$

Complete **table:**

Time, t /mins	0	30	60	90	120
ln [A]	2.16	1.88	1.59	1.30	1.01

- Plot ln [A] *along* y-axis; t *along* x-axis
- Is it linear? ***Yes.***
  - Calc. slope as: -0.00959 so **k =+9.6×10^{-3} min^{-1}**

Reaction Order by Integral Method



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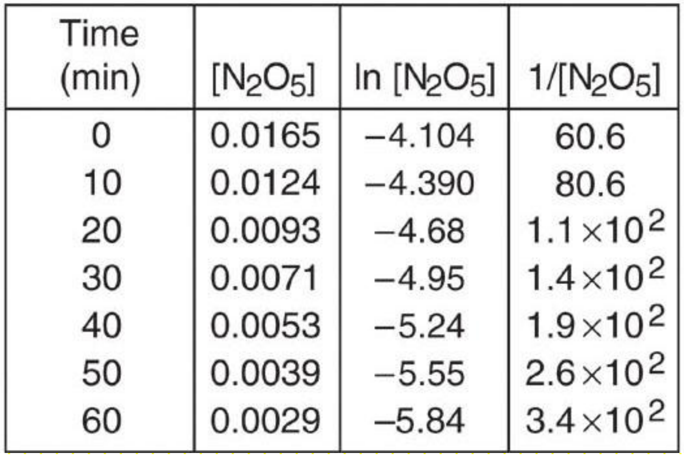
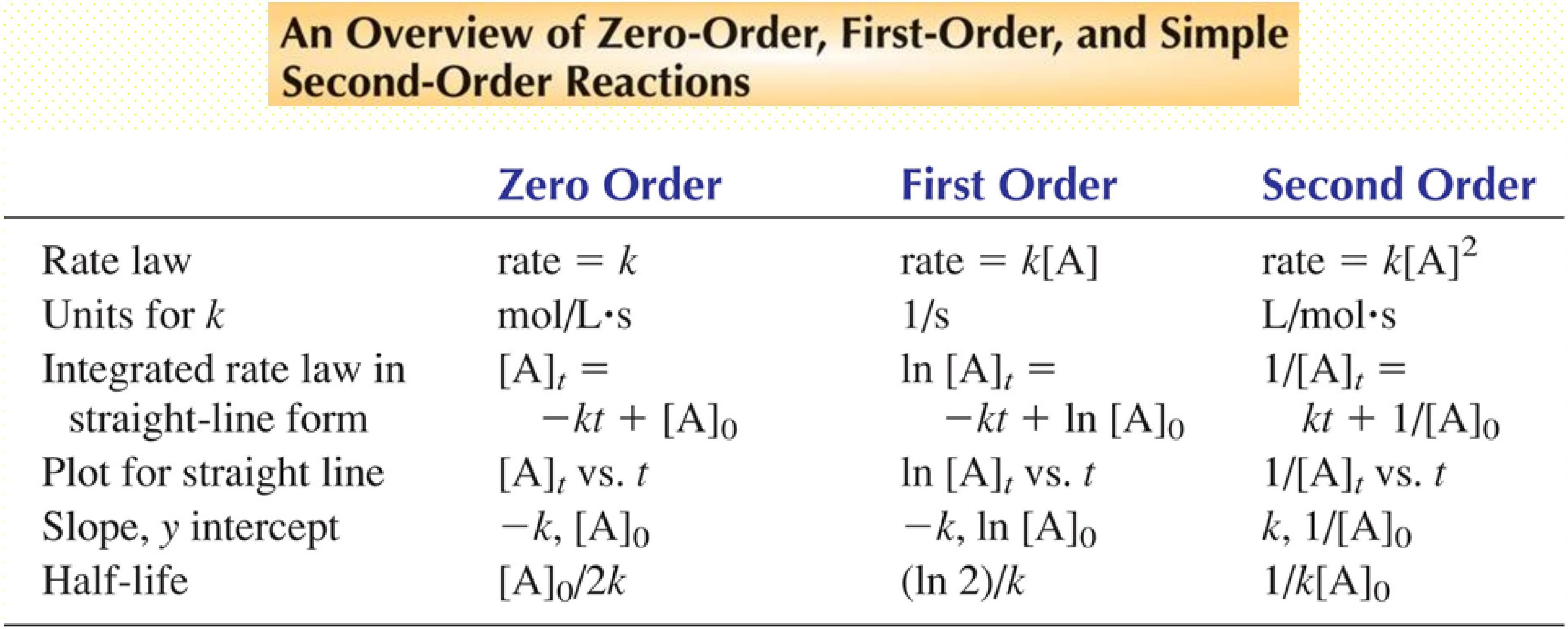


Time (min)	[N$_2$O$_5$]	ln [N$_2$O$_5$]	1/[N$_2$O$_5$]
0	0.0165	−4.104	60.6
10	0.0124	−4.390	80.6
20	0.0093	−4.68	1.1×10^2
30	0.0071	−4.95	1.4×10^2
40	0.0053	−5.24	1.9×10^2
50	0.0039	−5.55	2.6×10^2
60	0.0029	−5.84	3.4×10^2

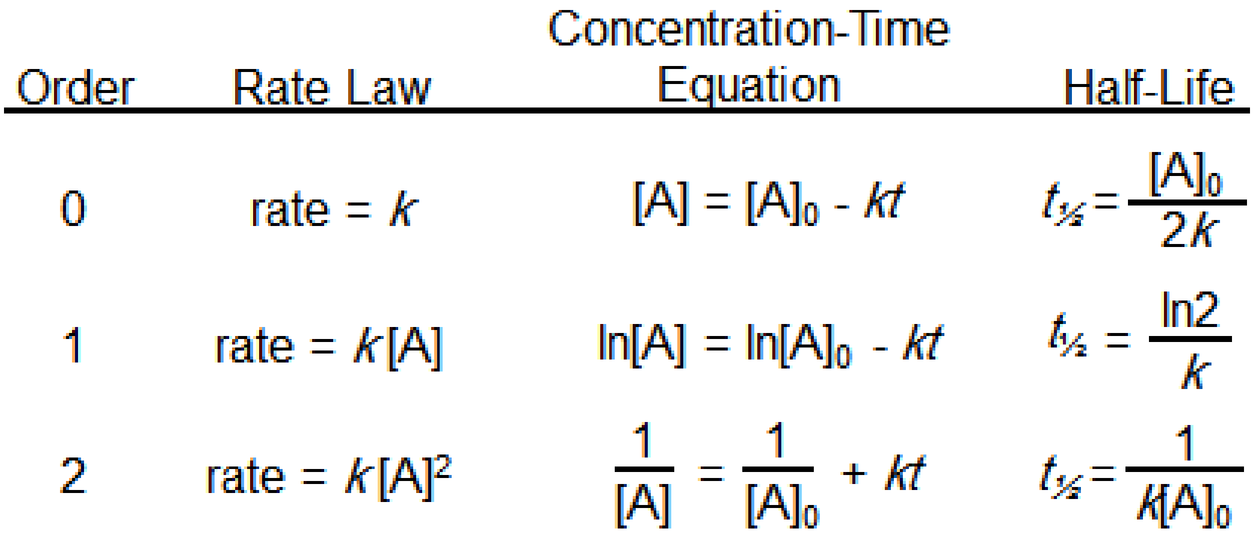
The concentration data is used to construct three different plots. Since the plot of ln [N_2O_5] vs. time gives a straight line, the reaction is first order.

Graphical determination of the reaction order for the decomposition of N_2O_5.



An Overview of Zero-Order, First-Order, and Simple Second-Order Reactions

	Zero Order	First Order	Second Order
Rate law	rate = k	rate = $k[A]$	rate = $k[A]^2$
Units for k	mol/L·s	1/s	L/mol·s
Integrated rate law in straight-line form	$[A]_t = -kt + [A]_0$	$\ln [A]_t = -kt + \ln [A]_0$	$1/[A]_t = kt + 1/[A]_0$
Plot for straight line	$[A]_t$ vs. t	$\ln [A]_t$ vs. t	$1/[A]_t$ vs. t
Slope, y intercept	$-k$, $[A]_0$	$-k$, $\ln [A]_0$	k, $1/[A]_0$
Half-life	$[A]_0/2k$	$(\ln 2)/k$	$1/k[A]_0$



Order	Rate Law	Concentration-Time Equation	Half-Life
0	rate = k	$[A] = [A]_0 - kt$	$t_{1/2} = \frac{[A]_0}{2k}$
1	rate = $k[A]$	$\ln[A] = \ln[A]_0 - kt$	$t_{1/2} = \frac{\ln 2}{k}$
2	rate = $k[A]^2$	$\frac{1}{[A]} = \frac{1}{[A]_0} + kt$	$t_{1/2} = \frac{1}{k[A]_0}$

Units of Rate Constants

Units of the Rate Constant *k* for Several Overall Reaction Orders

Overall Reaction Order	**Units of *k* (*t* in seconds)**
0	mol/L·s (or mol $L^{-1}s^{-1}$)
1	1/s (or s^{-1})
2	L/mol·s (or L $mol^{-1}s^{-1}$)
3	L^2/mol^2·s (or L^2 $mol^{-2}s^{-1}$)

General formula:

$$\text{Units of } k = \frac{\left(\frac{L}{mol}\right)^{\text{order}-1}}{\text{unit of } t}$$

2) Initial Rate Method

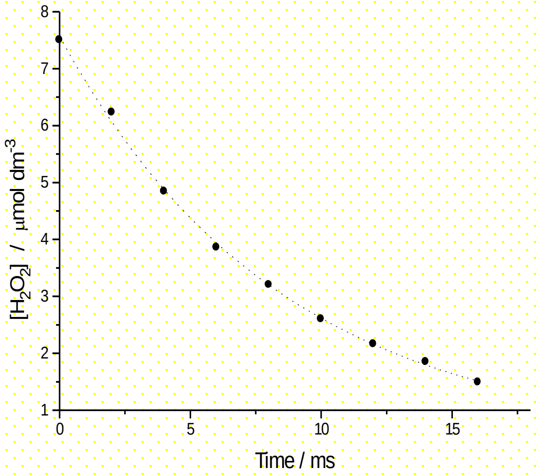
Method of Initial Rates

- Measure the rate of the reaction right at the start.
- Vary the starting concentrations
- Compare initial rates to initial concentrations

- Isolation of variables: Vary only one concentration at a time and keep temperature constant
- If concentration doubles and:
  - Rate does not change, then zero order
  - Rate doubles, then first order
  - Rate quadruples, then second order
- General Rule:

$$\frac{\text{Rate in experiment 2}}{\text{Rate in experiment 1}} = \frac{[A_2]^n}{[A_1]^n} = \left(\frac{[A_2]}{[A_1]}\right)^n$$

Initial Rate Method



$$5\ Br^- + BrO_3^- + 6\ H^+ \rightarrow 3\ Br_2 + 3\ H_2O$$

General reaction: $A + B + \ldots \rightarrow P + Q + \ldots$

- Rate law: $R = k\,[A]^a\,[B]^b \ldots$??

$$\log R_0 = a.\log[A]_0 + (\log k + b \log[B]_0 + \ldots)$$

$$\mathbf{y = m\,.\,x + c}$$

- Do series of expts. in which all $[B]_0$, etc. are constant and only $[A]_0$ is varied; measure R_0
- Plot $\log R_0$ (Y-axis) *versus* $\log [A]_0$ (X-axis)
- Slope = a (reaction order w.r.t. reactant “A”)
- Repeat making [B] variable & [A] constant, get “b”

Example: $R_0 = k\,[NO]^a[H_2]^b$

$$2\ NO + 2\ H_2 \rightarrow N_2 + 2\ H_2O$$

Expt	$[NO]_0$	$[H_2]_0$	R_0
1	**25**	**10**	**2.4×10^{-3}**
2	**25**	**5**	**1.2×10^{-3}**
3	**12.5**	**10**	**0.6×10^{-3}**

Deduce orders w.r.t. NO and H_2 and calculate k.

- *Compare* experiments #1 and #2 $\Rightarrow \beta$ (B variable)
- *Compare* experiments #1 and #3 $\Rightarrow \alpha$ (A variable)
- Solve for k from $k = R_0 / ([NO]^{\alpha}[H_2]^{\beta})$

How to measure initial rate?

- Key: - (d[A]/dt) » - (d[A]/dt) » (d[P]/dt)

A + B + … → P + Q + …

t = 0 100 100 → 0 0 mol m^{-3}

10 s 99 99 → 1 1 (same units)

- Rate? (100-99)/10 = -0.10 mol m^{-3} s^{-1}

OR: +(0-1)/10 = -0.10 mol m^{-3} s^{-1}

Example: Determining Reaction Orders

- For the general reaction A + 2B → C + D, the rate law will have the form: **Rate = $k\,[A]^m\,[B]^n$**
- To determine the values of *m* and *n*, we run a series of experiments in which one reactant concentration changes while the other is kept constant, and we measure the effect on the initial rate in each case.

Table 16.2 Initial Rates for the Reaction between A and B

Experiment	Initial Rate (mol/L·s)	Initial [A] (mol/L)	Initial [B] (mol/L)
1	1.75×10^{-3}	2.50×10^{-2}	3.00×10^{-2}
2	3.50×10^{-3}	5.00×10^{-2}	3.00×10^{-2}
3	3.50×10^{-3}	2.50×10^{-2}	6.00×10^{-2}
4	7.00×10^{-3}	5.00×10^{-2}	6.00×10^{-2}

[B] is kept constant for experiments 1 and 2, while [A] is doubled. Then [A] is kept constant while [B] is doubled.

Example:

Finding *m*, the order with respect to A:

We compare experiments 1 and 2, where [B] is kept constant but [A] doubles:

$$\frac{\text{Rate 2}}{\text{Rate 1}} = \frac{\cancel{k}[A]_2^m \cancel{[B]}_2^n}{\cancel{k}[A]_1^m \cancel{[B]}_1^n} = \frac{[A]_2^m}{[A]_1^m} = \left(\frac{[A]_2}{[A]_1}\right)^m$$

$$\frac{3.50\text{x}10^{-3}\ \text{mol/L}\cdot\text{s}}{1.75\text{x}10^{-3}\text{mol/L}\cdot\text{s}} = \left(\frac{5.00\text{x}10^{-2}\ \text{mol/L}}{2.50\text{x}10^{-2}\ \text{mol/L}}\right)^m$$

Dividing, we get $2.00 = (2.00)^m$ so $m = 1$

Example:

Finding *n*, the order with respect to B:

We compare experiments 3 and 1, where [A] is kept constant but [B] doubles:

$$\frac{\text{Rate 3}}{\text{Rate 1}} = \frac{\cancel{k[A]_3^m}\,[B]_3^n}{\cancel{k[A]_1^m}\,[B]_1^n} = \frac{[B]_3^n}{[B]_1^n} = \left(\frac{[B]_3}{[B]_1}\right)^n$$

$$\frac{3.50\text{x}10^{-3}\ \text{mol/L}\cdot\text{s}}{1.75\text{x}10^{-3}\text{mol/L}\cdot\text{s}} = \left(\frac{6.00\text{x}10^{-2}\ \text{mol/L}}{3.00\text{x}10^{-2}\ \text{mol/L}}\right)^m$$

Dividing, we get 2.00 = $(2.00)^n$ so $n = 1$

3) Isolation

$$IO_3^- + 8\ I^- + 6\ H^+ \rightarrow 3\ I_3^- + 3\ H_2O$$

- Rate = k $[IO_3^-]^\alpha\ [I^-]^\beta\ [H^+]^\gamma$
  - Add excess iodate to reaction mix
    - » Hence $[IO_3^-]$ is *effectively* constant
  - Rate = k′ $[I^-]^\beta\ [H^+]^\gamma$
  - Add excess acid
    - » Therefore $[H^+]$ is *effectively* constant
- Rate ≈ k″ $[I^-]^\beta$
- Use integral or initial rate methods *as appropriate.*

Effect of Temperature on reaction rates:

Arrhenius law & Activation energy, Collision and Transition State Theories

Arrhenius Law of Chemical Kinetics

- Temperature has a dramatic effect on reaction rate.
- For many reactions, an increase of 10 °C will double or triple the rate.
- Experimental data shows that k increases exponentially as T increases. This is expressed in the Arrhenius equation:

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

$$\ln k = \ln A - E_a / RT$$

k is the rate constant, E_a is the activation energy,

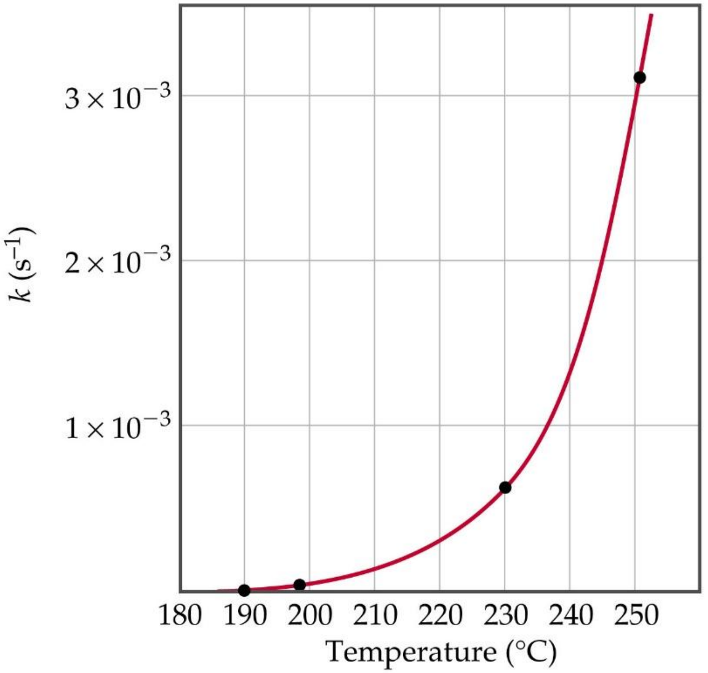
R is the gas constant (8.314 J/mol-K) and T is the absolute temperature in K.

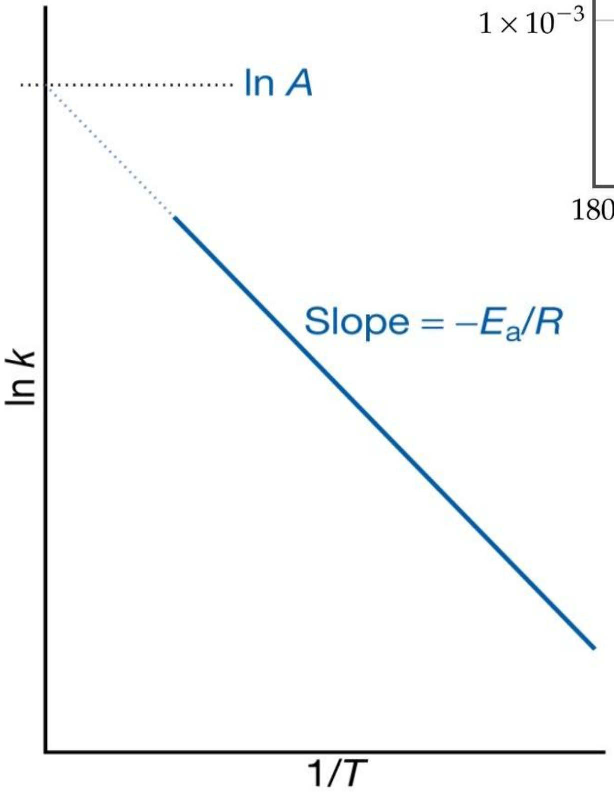
A is called the frequency (pre-exponential) factor. A is a measure of the probability of favorable collisions.

Both A and E_a are specific to a given reaction.

Arrhenius Law

1. Rates of most chemical reactions increase with temperature.
2. In some cases the rate constant may appear to decrease with temperature but this is because it is a combination of 2 or more rate constants e.g., k1/k2.
3. The rate law does not change but the rate constant increases with temperature.





To determine E_a from a set of data, plot ln k vs 1/T:
Slope = $-E_a/R$;
Intercept = ln A

Calculating Activation Energy from two data points

- E_a can be calculated from the Arrhenius equation:

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

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

straight-line form

- If data is available at two different temperatures:

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

Calculating Activation Energy from 2 data points

Example:

The decomposition of hydrogen iodide: $2HI(g) \rightarrow H_2(g) + I_2(g)$ has rate constants of 9.51×10^{-9} L/mol·s at 500. K and 1.10×10^{-5} L/mol·s at 600. K. Find E_a.

SOLUTION:

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

$$E_a = -(8.314\ \text{J/mol·K})\ \ln\left(\frac{1.10 \times 10^{-5}\ \text{L/mol·s}}{9.51 \times 10^{-9}\ \text{L/mol·s}}\right)\left(\frac{1}{600.\text{K}} - \frac{1}{500.\ \text{K}}\right)^{-1}$$

$$= 1.76 \times 10^{5}\ \text{J/mol} = 1.76 \times 10^{2}\ \text{kJ/mol}$$

Collision Theory of Reaction Kinetics

1. Molecules must collide before they can react.
2. They must do so in the correct orientation (see next)
3. In a gas, molecules are traveling with different velocities and have different kinetic energies. The average kinetic energy is dependent on temperature (Kinetic Theory of Gases).
4. Colliding molecules must together have enough kinetic energy to break existing bonds.
5. The minimum kinetic energy required for a reaction to occur is the **activation energy**, $\mathbf{E_{a.}}$ They must collide with an energy greater than the “activation” energy.

Effect of Temperature on reaction rates

increased T → increased average speed of particles → increased collision frequency → increased reaction rate

- Most collisions fail to yield products because of:
  1. activation energy factor: only those collisions with energy equal to, or greater than, E_a can yield products. Increasing **T** enhances the fraction of productive collisions, **f**. From the equation below, we can see that both **E_a** and **T** affect **f**, which in turn influences reaction rate:

$$\boxed{f = e^{-E_a/RT}}$$

  2. Molecular orientation factor. In order for reaction to occur, the reactant molecules (with enough energy to form products) must collide in the correct orientation.

Effective Collisions:

Collisions that result in a chemical reaction are called ***effective collisions***.

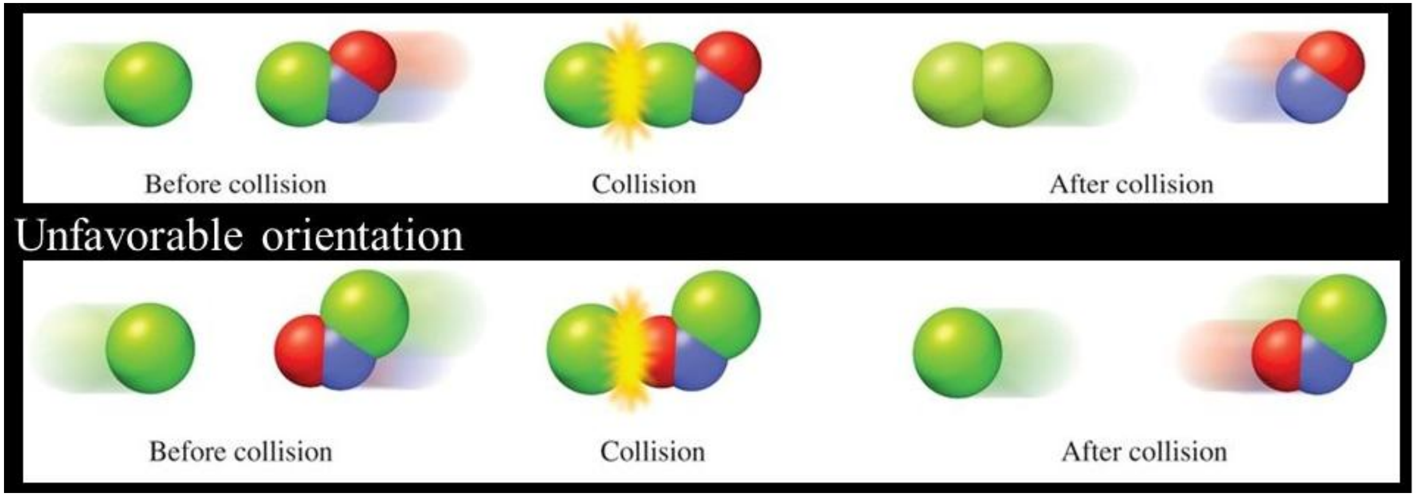
The ***activation energy*** (***E_a***) is the minimum amount of energy required to initiate a chemical reaction.

Molecules must also be oriented in a way that favors reaction.

$$\mathrm{Cl} + \mathrm{NOCl} \rightarrow \mathrm{Cl_2} + \mathrm{NO}$$

Incorrect orientation does not favor reaction

An ineffective collision results in no reaction.

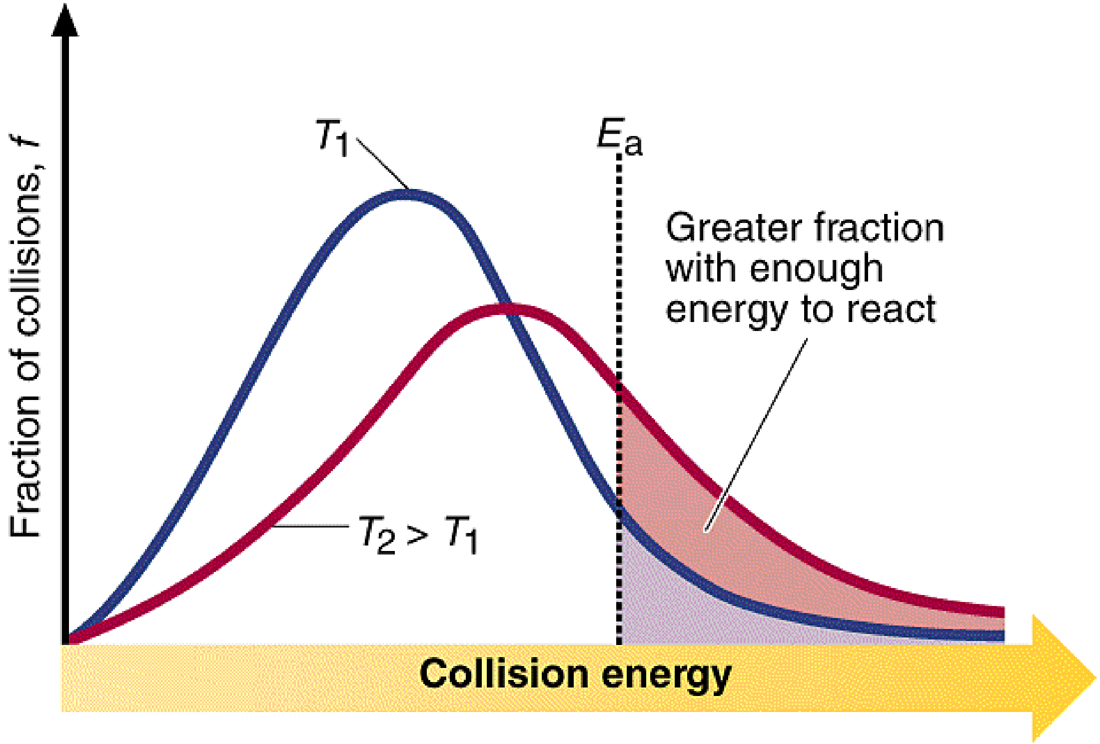


Collision Theory: Activation Energy

- We can show the fraction of molecules, f, with energy equal to or greater than Ea is:

$$f = e^{-E_a/RT}$$

where R is the gas constant (8.314 J/mol·K).



Activation Energy

Effect of E_a and T on the Fraction (f) of Collisions with Sufficient Energy to Allow Reaction

E_a (kJ/mol)	**f (at T = 298 K)**
50	1.70x10^{-9}
75	7.03x10-14
100	2.90x10^{-18}
T	**f (at E_a = 50 kJ/mol)**
25° C (298 K)	1.70x10^{-9}
35° C (308 K)	3.29x10^{-9}
45° C (318 K)	6.12x10^{-9}

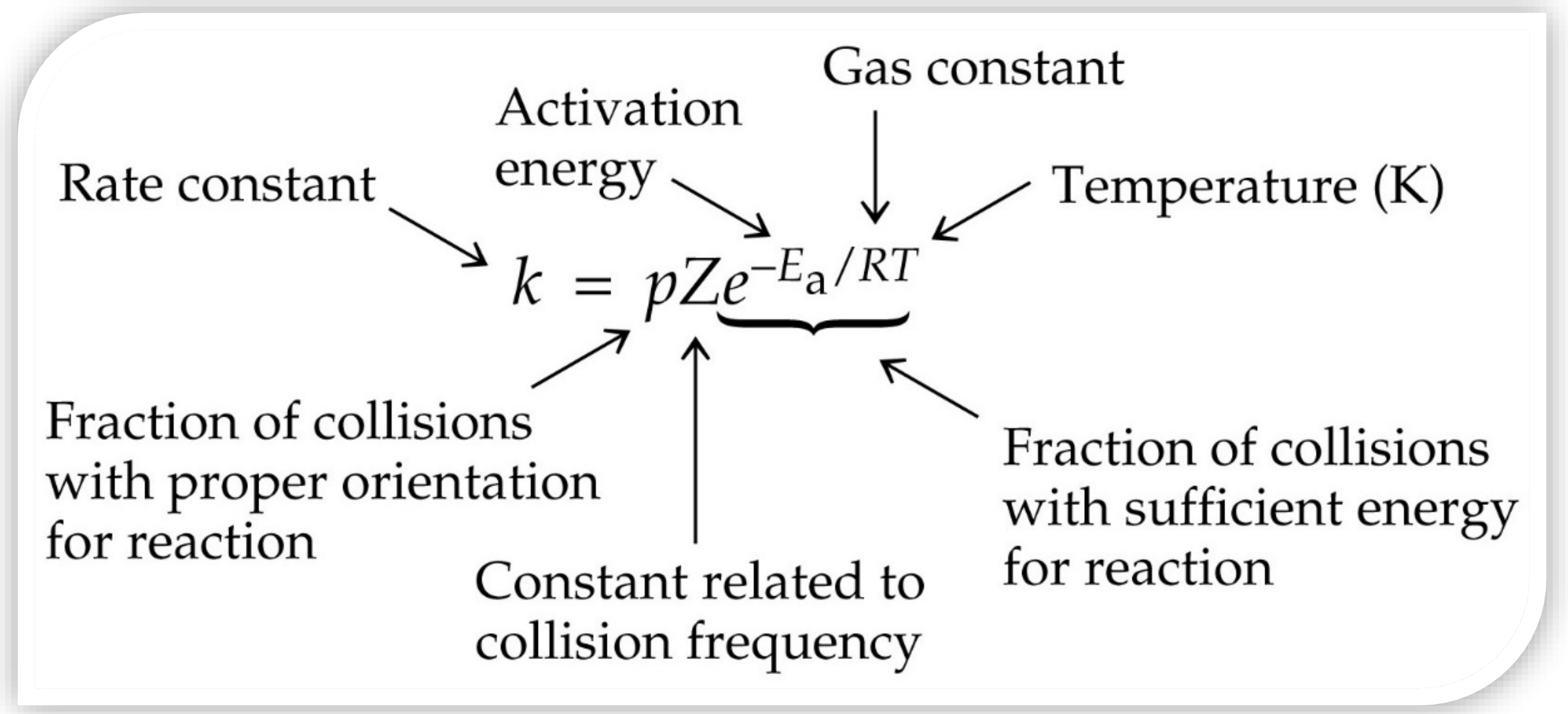
Collision Theory and the Rate Constant

- For elementary processes "Rate = k[A][B]"; the following expression for reaction rate constant applies: **$k = p \times Z \times f$**

Where the fraction of collisions with sufficient energy is:

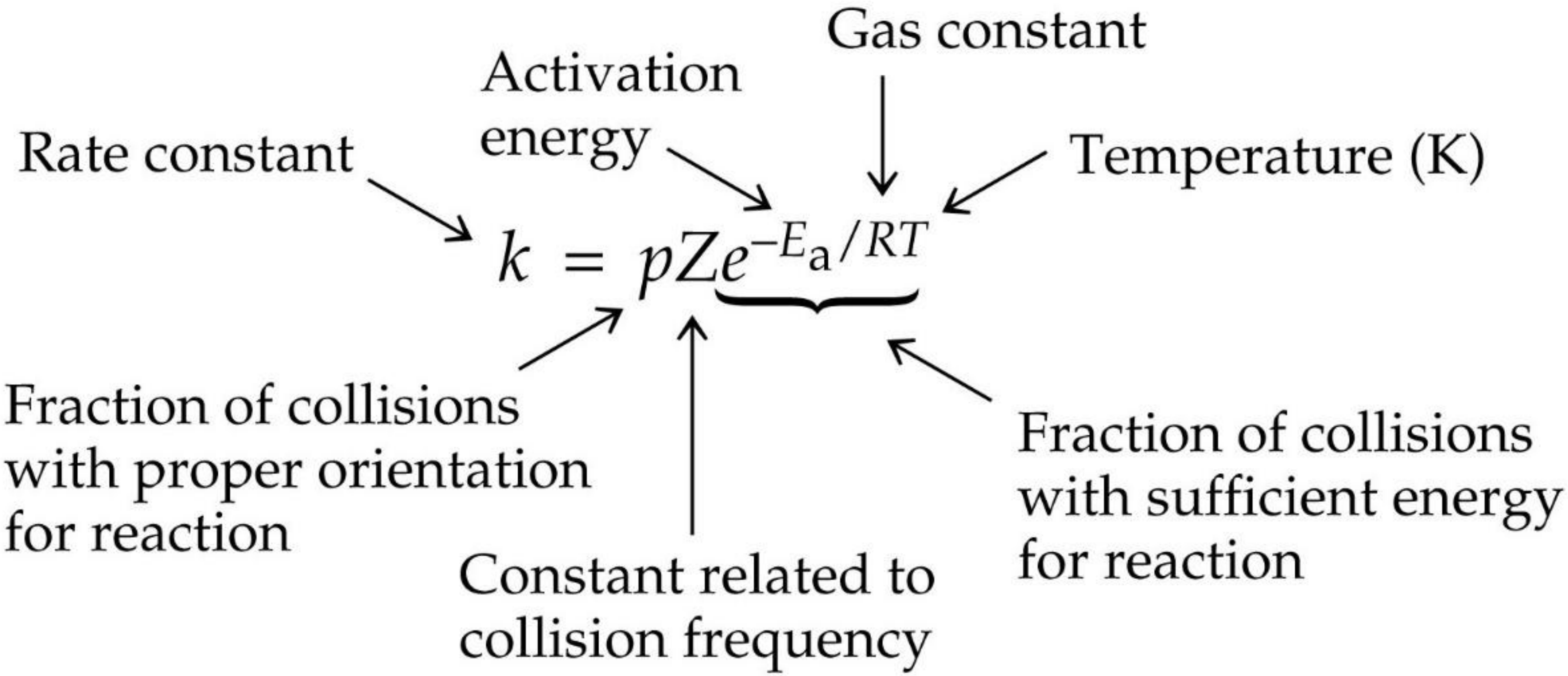
$$\mathbf{f = e^{-Ea/RT}}$$

Thus:



Collision Theory and the Rate Constant

- Substitute into the collision theory equation for the rate constant:



Gas constant

Activation energy

Rate constant

Temperature (K)

$$k = pZ\underbrace{e^{-E_a/RT}}$$

Fraction of collisions with proper orientation for reaction

Constant related to collision frequency

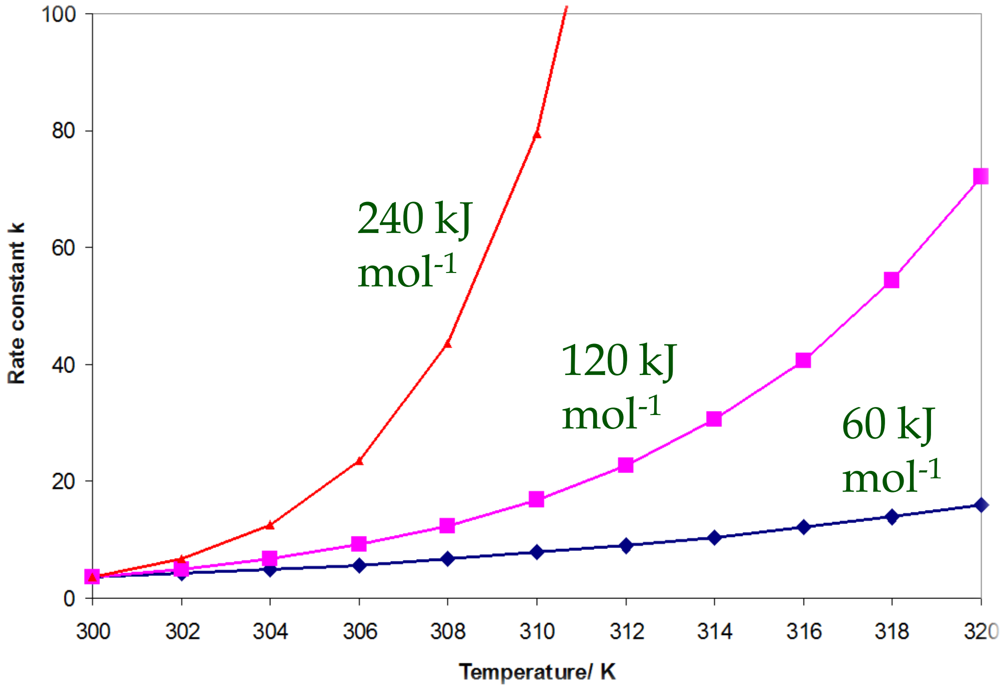
Fraction of collisions with sufficient energy for reaction

- The larger the activation energy, the smaller the fraction of molecules having enough energy to react, so the slower the rate

Activation Energy & Temperature

- The higher the activation energy, the more sensitive the reaction rate is to temperature.
- If the activation energy is low then the reaction rate increases slowly with temperature.
- Some radical recombination reactions have zero activation energy (i.e., non-activated): *The rate is largely temperature independent.*

- **Try out some plots on an Excel spreadsheet.**
- **See how variation of E_a causes the rate-constant to become more sensitive to temperature.**



Ea → 0   No Temp effect

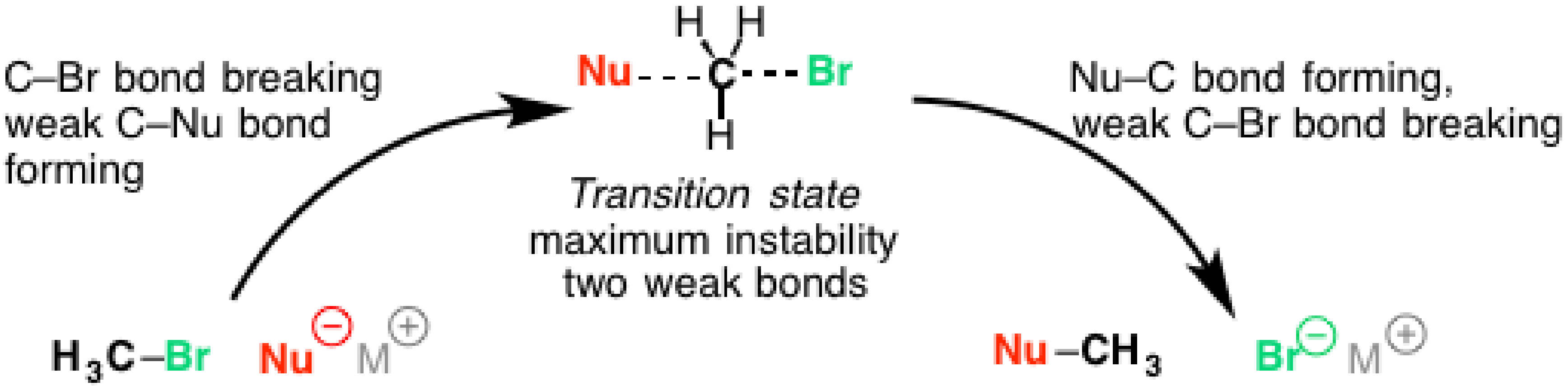
Arrhenius parameters for selected reactions

1st order reactions	A / s^{-1}	E / kJ mol^{-1}
$2\ N_2O_5\ (g) \rightarrow 4\ NO_2\ (g) + O_2\ (g)$	4.94×10^{13}	103
cyclopropane (g) → propene (g)	1.58×10^{15}	272
cyclobutane (g) → $2\ C_2H_4$ (g)	3.98×10^{13}	261
$C_2H_6\ (g) \rightarrow 2CH_3\bullet\ (g)$	2.51×10^{7}	384
2nd order reactions (gas-phase)	A / L mol^{-1} s^{-1}	E / kJ mol^{-1}
$2CH_3\bullet\ (g) \rightarrow C_2H_6\ (g)$	2×10^{10}	~0
$NO\ (g) + Cl_2\ (g) \rightarrow NOCl\ (g) + Cl\ (g)$	4.0×10^{9}	85
$O\ (g) + N_2\ (g) \rightarrow NO\ (g) + N\ (g)$	1×10^{11}	315
2nd order reactions (solution)	A / L mol^{-1} s^{-1}	E / kJ mol^{-1}
$CO_2 + OH^- \rightarrow HCO_3^-$ (water)	1.5×10^{10}	38
$C_2H_5ONa + CH_3I \rightarrow C_2H_5OH + NaI$ (ethanol)	2.42×10^{11}	81.6
$(CH_3)_3CCl + H_2O \rightarrow (CH_3)_3OH + HCl$ (water)	7.1×10^{16}	100

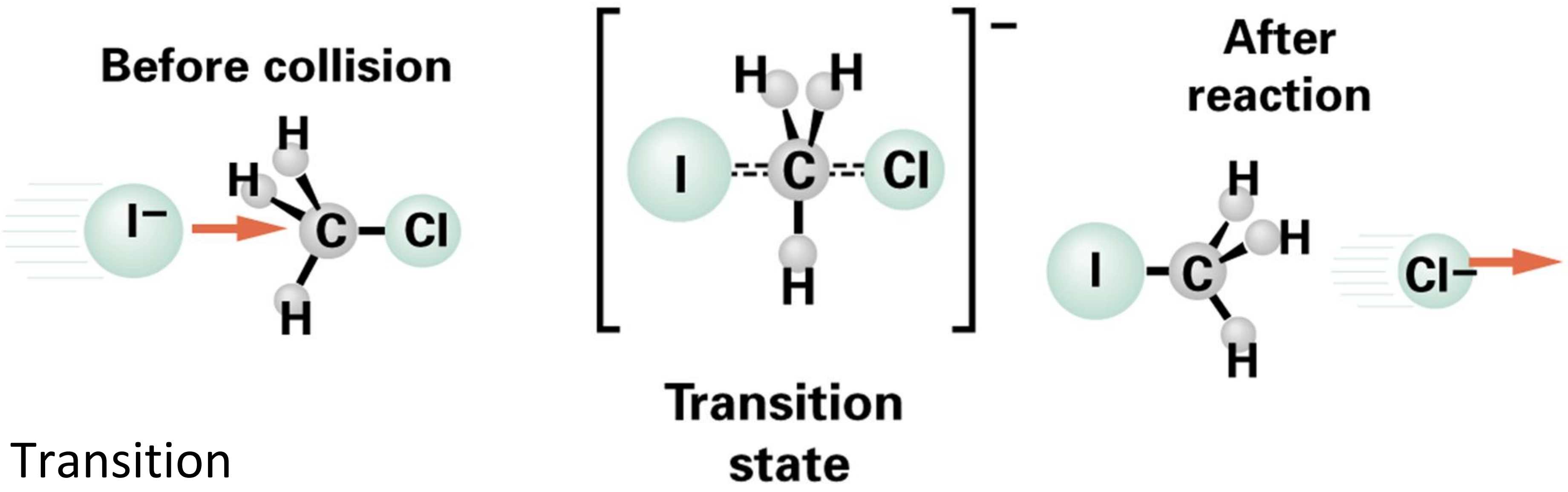
Data: 'Physical chemistry', P.W. Atkins

Transition State Theory

1. At the moment of collision, molecules with enough energy and the right orientation combine to form an activated complex
2. The activated complex can either revert back to reactants or decompose to products
3. The exact nature of the activated complex is difficult to determine
4. Less energy is required to form an activated complex than to beak bonds.
5. Activation Energy is the difference between energies of the activated complex and reactants.

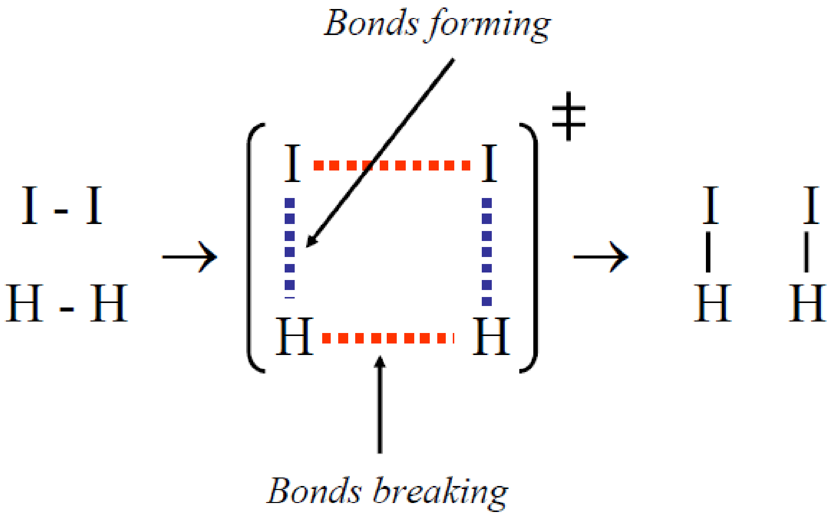


Transition State Theory



Transition state during chemical reactions

<u>Transition state</u> - bonds between reactants are breaking at the same time that bonds are forming between the products

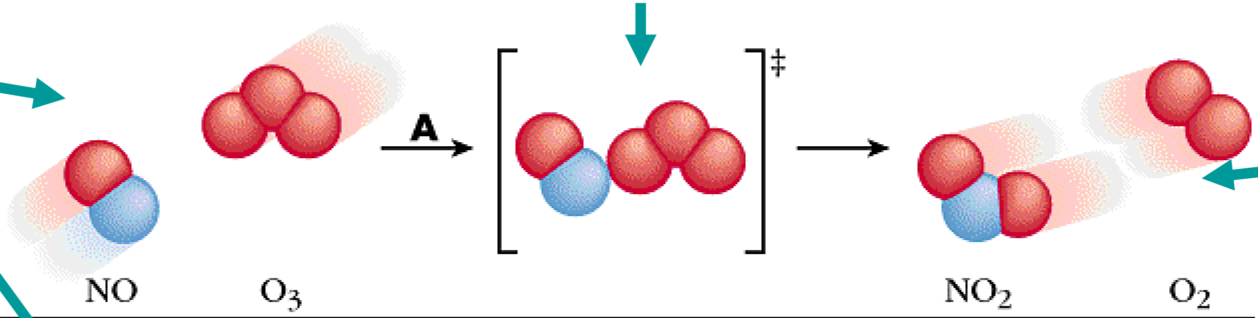


Transition State & Collision Theories

Reactants

Activated complex or transition state.

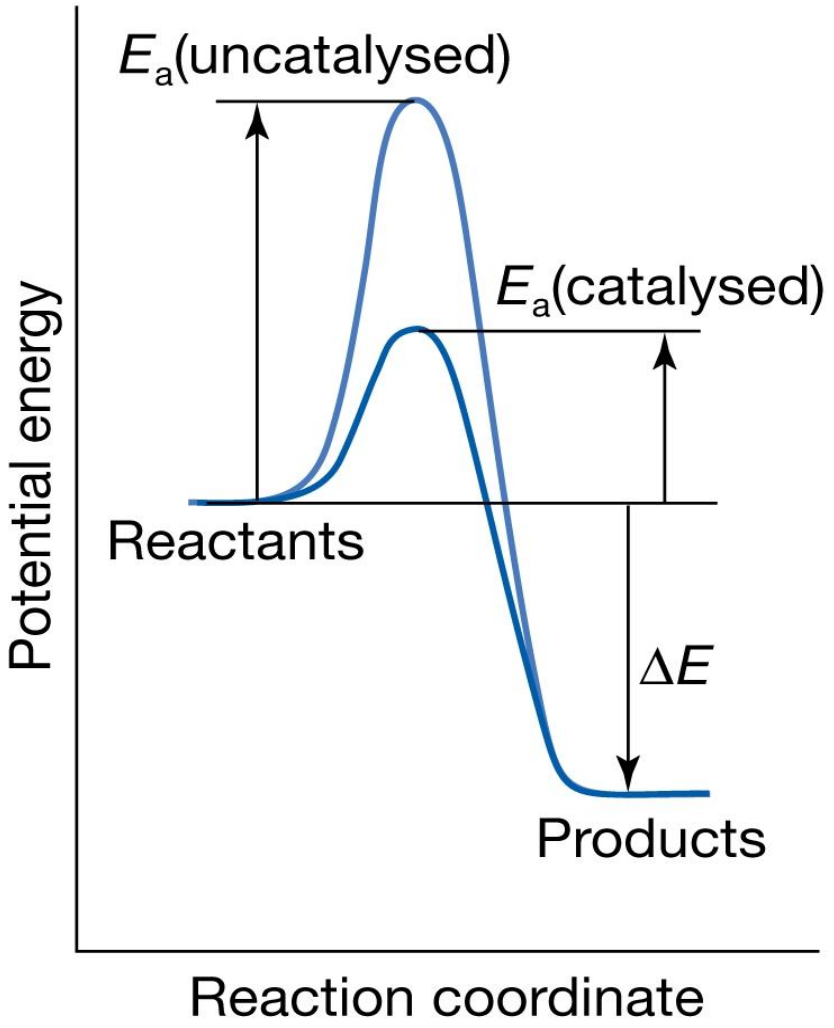
Products



$$\mathrm{NO} + \mathrm{O_3} \rightarrow \mathrm{NO_2} + \mathrm{O_2}$$

Activated Complex is NOT in equation!

Catalysis



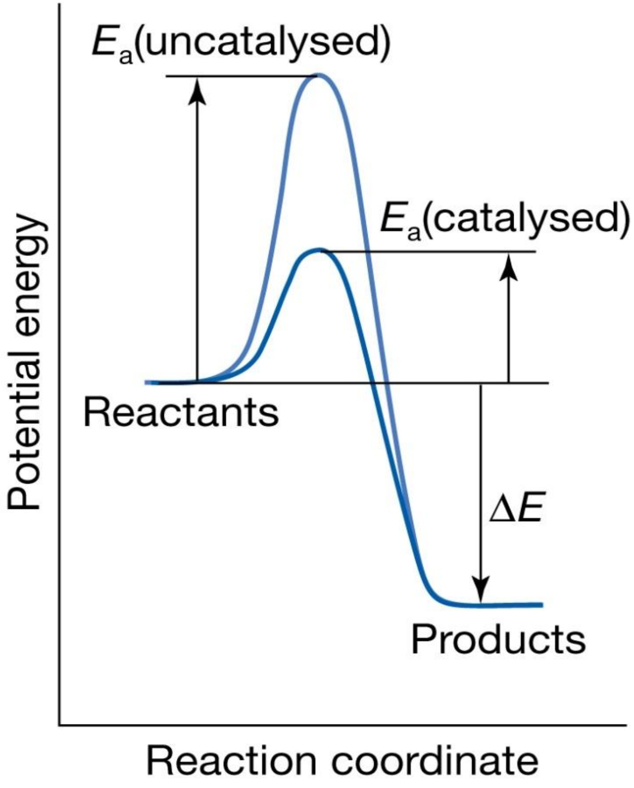
- A catalyst provides a reaction with an alternate pathway that has a lower energy of activation.

- The catalyst is not consumed in a reaction.

- The catalyst only speeds the reaction up.
- Enzymes are biological catalysts

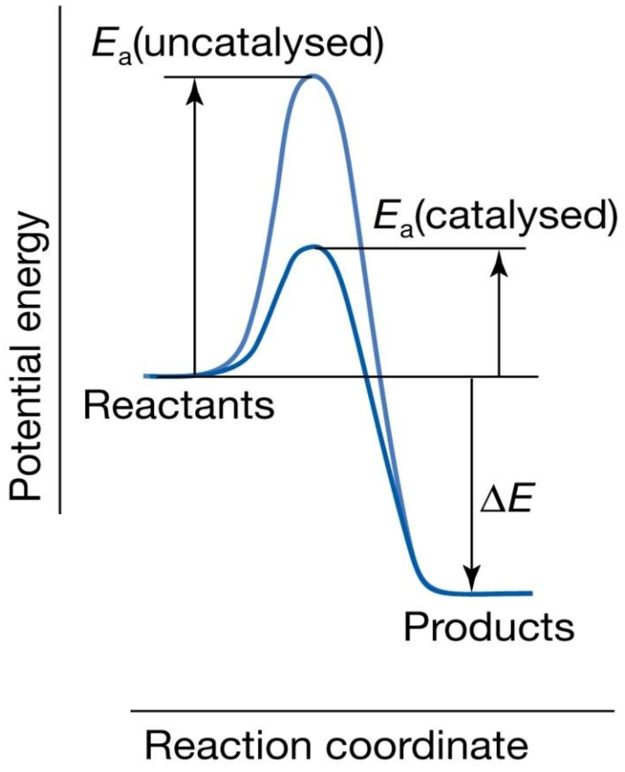
Catalysis

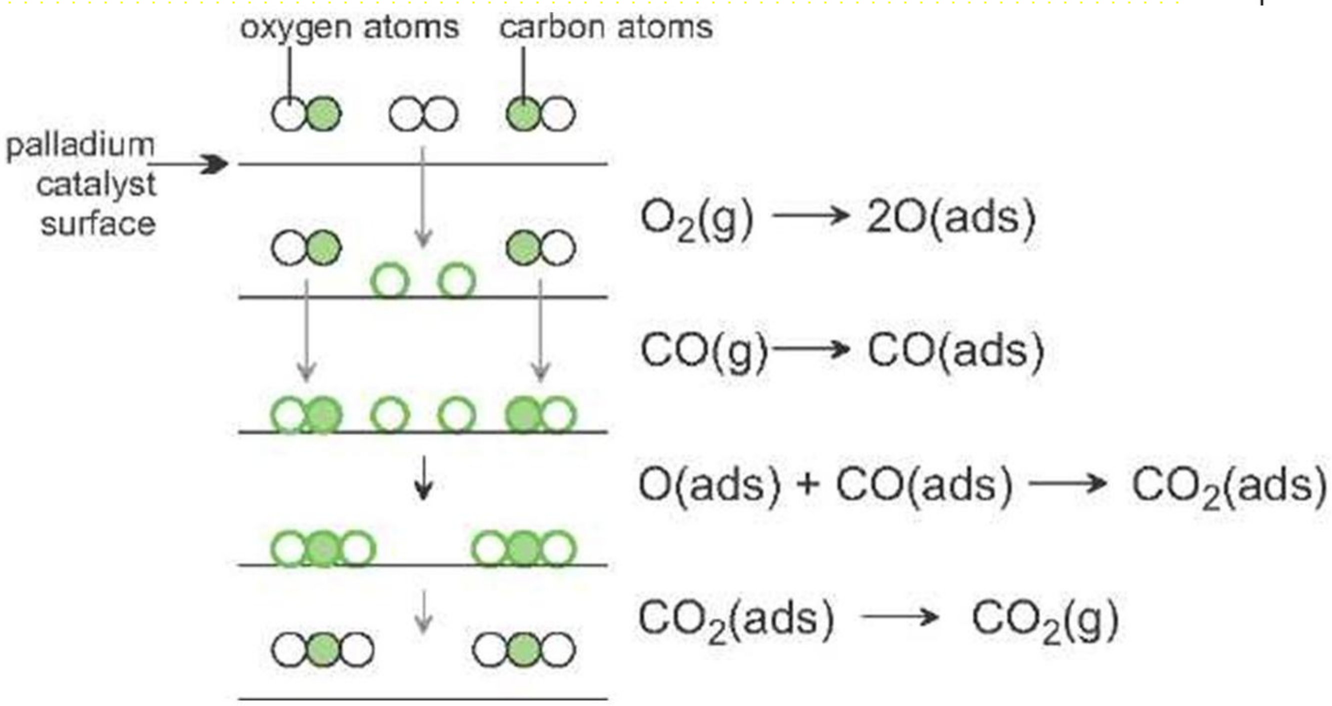
1. A catalyst provides a reaction with an alternate pathway that has a lower energy of activation.
   - Without catalyst, reactants molecules require more kinetic energy to make collisions with each other. Energy is usually provided as heat by increasing temperature.
   - Being adsorbed at catalyst surface, reactants molecules are closer to each other and thus interacts with less kinetics energy.
2. The catalyst is not consumed in a reaction.
3. The catalyst only speeds the reaction up.



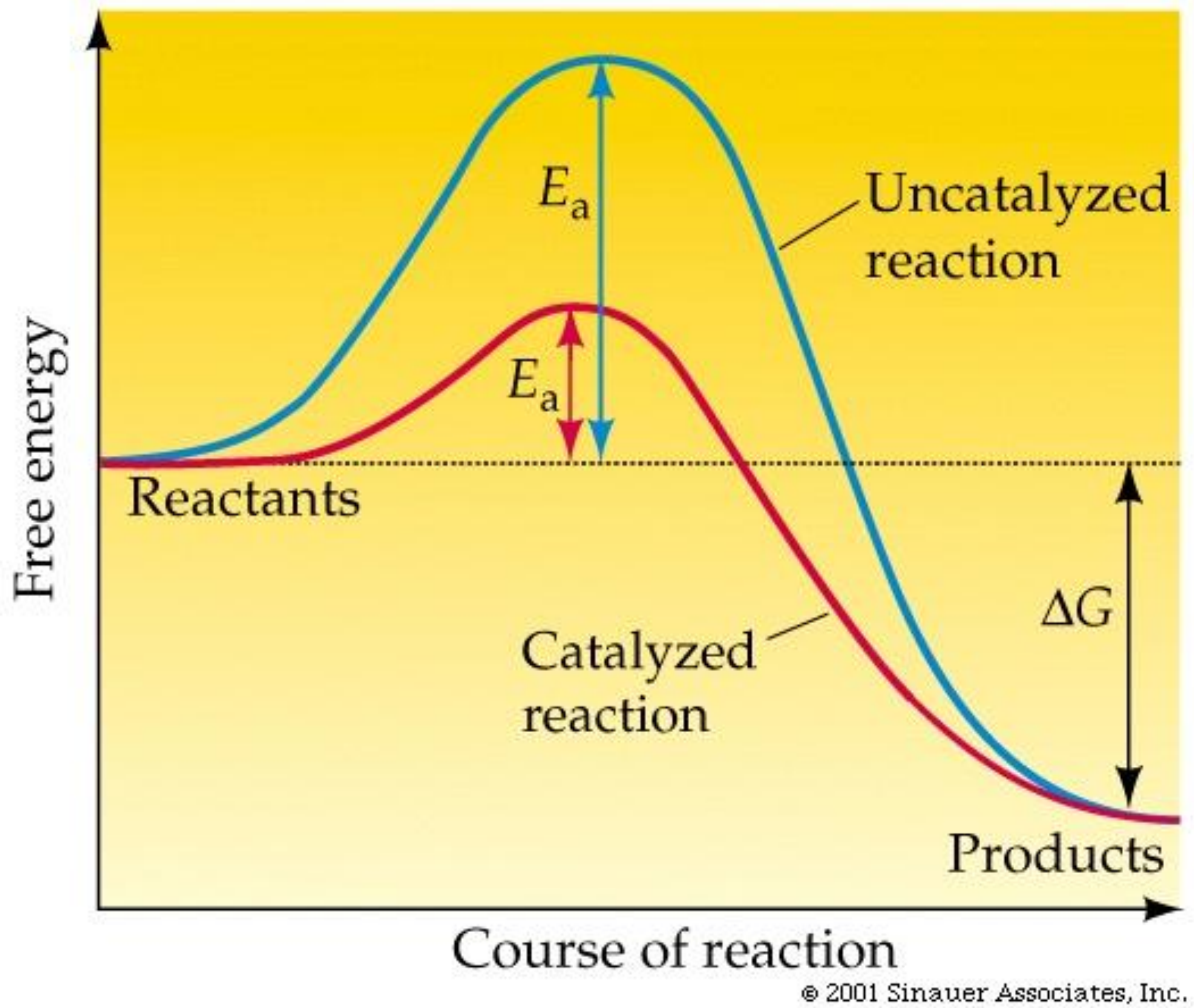
Catalysis

Example on the alternative pathway of reaction in presence of catalyst: (Reaction of adsorbed molecules)





Catalysis



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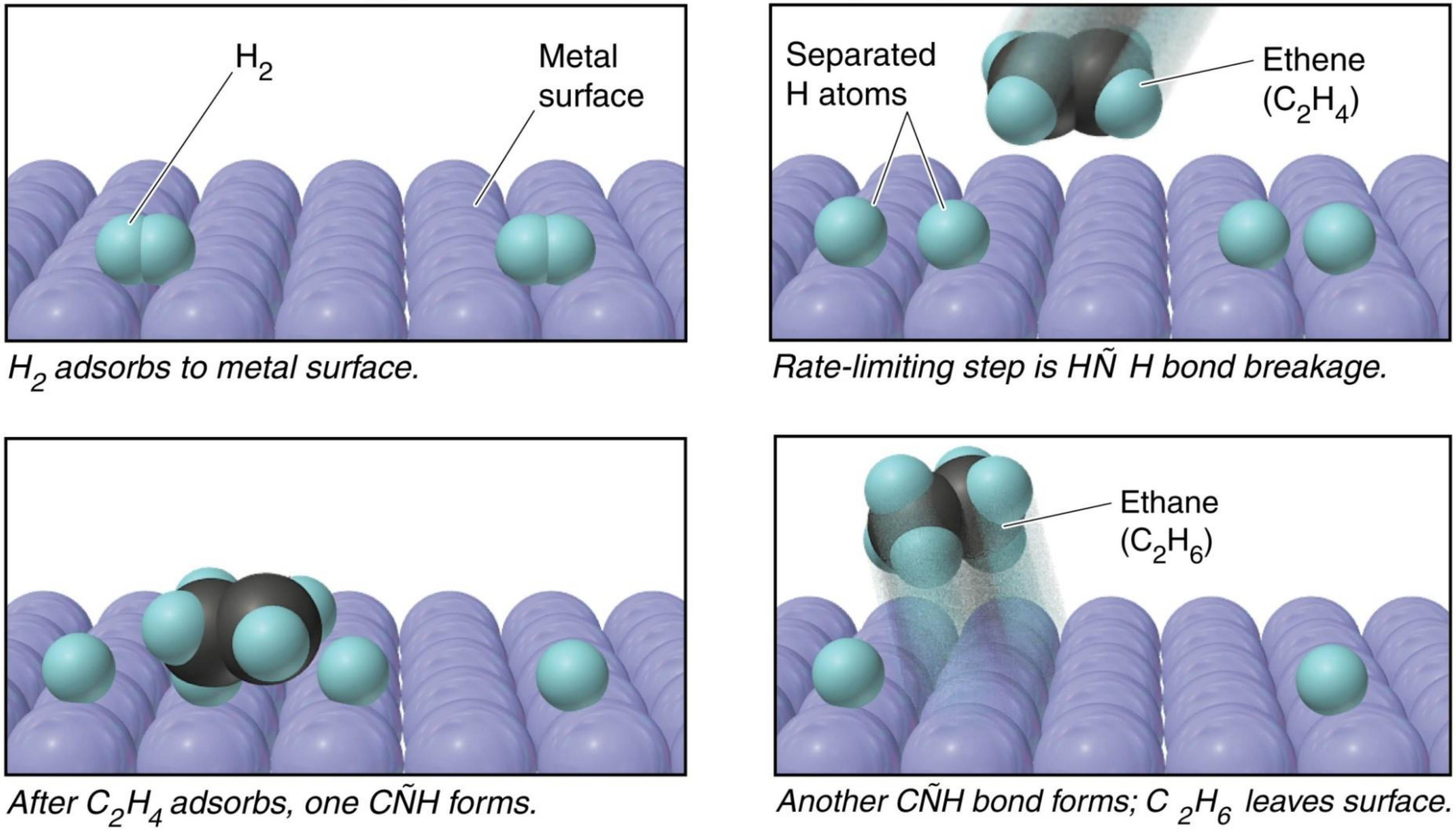
Catalysis



H_2 adsorbs to metal surface.

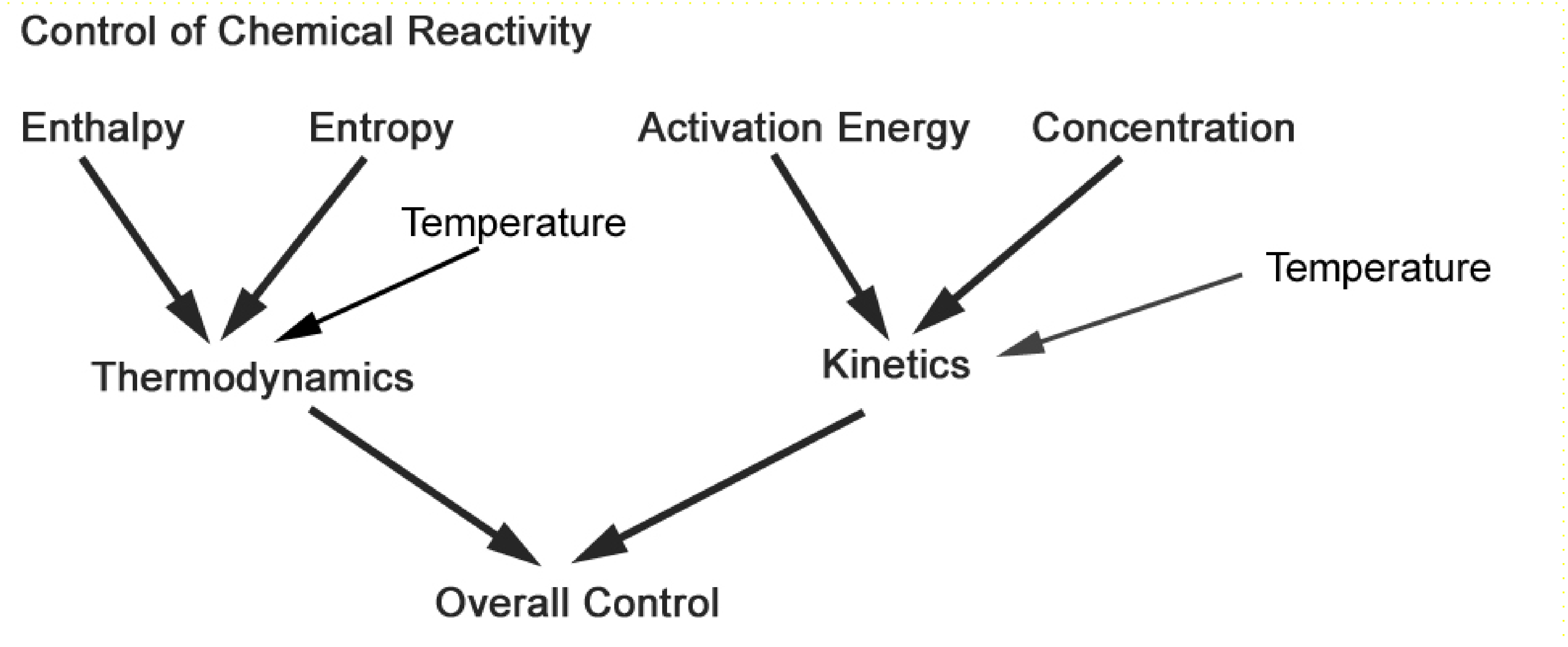
Rate-limiting step is HÑ H bond breakage.

After C_2H_4 adsorbs, one CÑH forms.

Another CÑH bond forms; C_2H_6 leaves surface.

The metal catalyst for the hydrogenation of ethane reaction.

Overall: Control of Reactivity



Control of Chemical Reactivity

Enthalpy

Entropy

Temperature

Activation Energy

Concentration

Temperature

Thermodynamics

Kinetics

Overall Control

$$Rate = Ae^{-\frac{Ea}{RT}}\,[reactants]^{order}$$