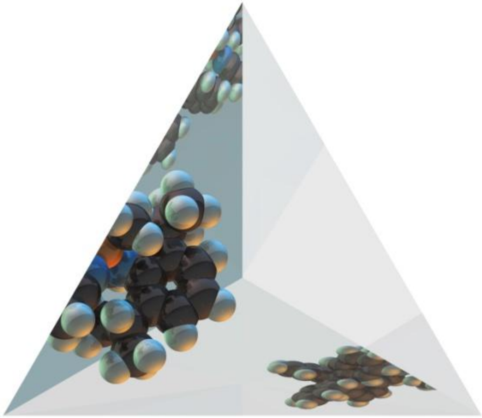

CHEMISTRY

The Central Science

8th Edition

Chapter 14
Chemical Kinetics

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Chemical Kinetics

- Chemical kinetics is the study of how rapidly *chemical reactions* occur.
- rate at which a chemical process occurs.
- Reaction rates depends on
  - The *concentrations* of the reactants
  - *Temperature*
  - The presence of a *catalyst*
  - *Surface area*

Factors Affecting Reaction Rate: Nature of the Reactants

- Nature of the reactants means what kind of reactant molecules and what physical condition they are in
  - small molecules tend to react faster than large molecules
  - gases tend to react faster than liquids, which react faster than solids
  - powdered solids are more reactive than “blocks”
    - more surface area for contact with other reactants
  - certain types of chemicals are more reactive than others
    - e.g. potassium metal is more reactive than sodium
  - ions react faster than molecules
    - no bonds need to be broken

Factors Affecting Reaction Rate: Temperature

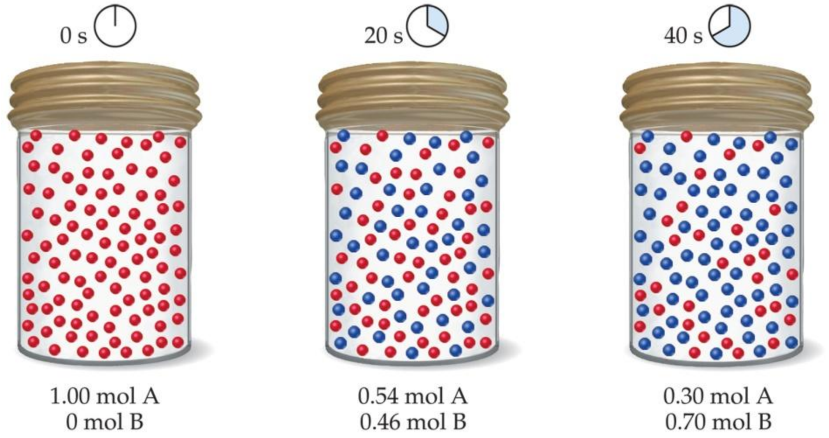
- Increasing temperature increases reaction rate
  - chemist’s rule of thumb—for each 10 °C rise in temperature, the speed of the reaction doubles
    - for many reactions
- There is a mathematical relationship between the absolute temperature and the speed of a reaction discovered by Svante Arrhenius, which will be examined later

Factors Affecting Reaction Rate: Catalysts

- Catalysts are substances that affect the speed of a reaction **without being consumed**
- Most catalysts are used to speed up a reaction; these are called positive catalysts
  - catalysts used to slow a reaction are called negative catalysts.
- Homogeneous = present in same phase
- Heterogeneous = present in different phase

Factors Affecting Reaction Rate: Reactant Concentration

- Generally, the larger the concentration of reactant molecules, the faster the reaction
  - increases the frequency of reactant molecule contact
  - concentration of gases depends on the partial pressure of the gas
    - higher pressure = higher concentration
- Concentrations of solutions depend on the solute-to-solution ratio (molarity)



Reaction Rates

Rates of reactions can be determined by *monitoring* the change in *concentration* of either *reactants* or *products* as a function of time.

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

$$= \frac{\Delta(\text{moles})}{\Delta t}$$

$$Br_2(aq) + HCOOH(aq) \longrightarrow 2Br^-(aq) + 2H^+(aq) + CO_2(g)$$

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

Reaction Rates

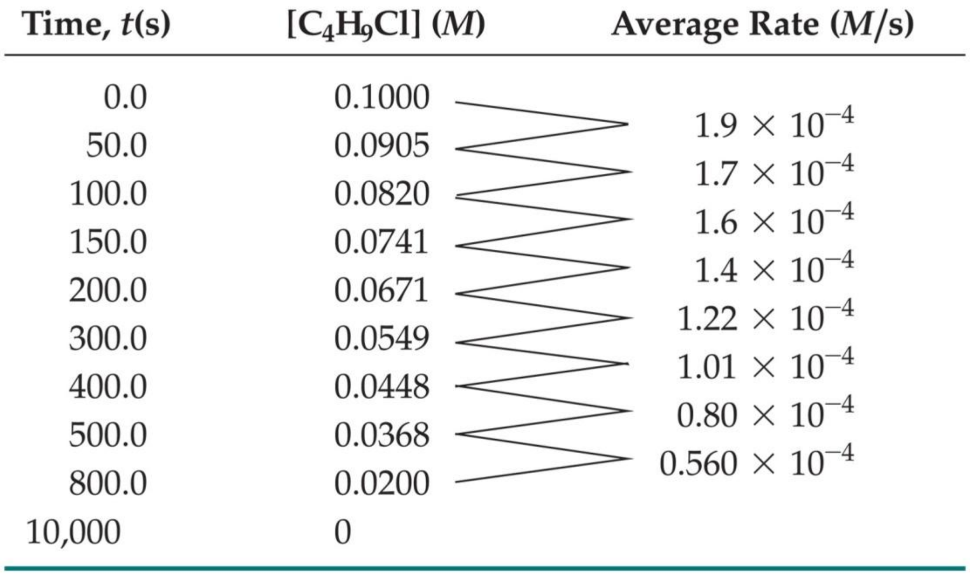
$$C_4H_9Cl(aq) + H_2O(l) \longrightarrow C_4H_9OH(aq) + HCl(aq)$$

Time, t(s)	$[C_4H_9Cl]$ (M)
0.0	0.1000
50.0	0.0905
100.0	0.0820
150.0	0.0741
200.0	0.0671
300.0	0.0549
400.0	0.0448
500.0	0.0368
800.0	0.0200
10,000	0

In this reaction, the concentration of *butyl chloride*, C_4H_9Cl, was *measured* at various *times*.

Reaction Rates

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



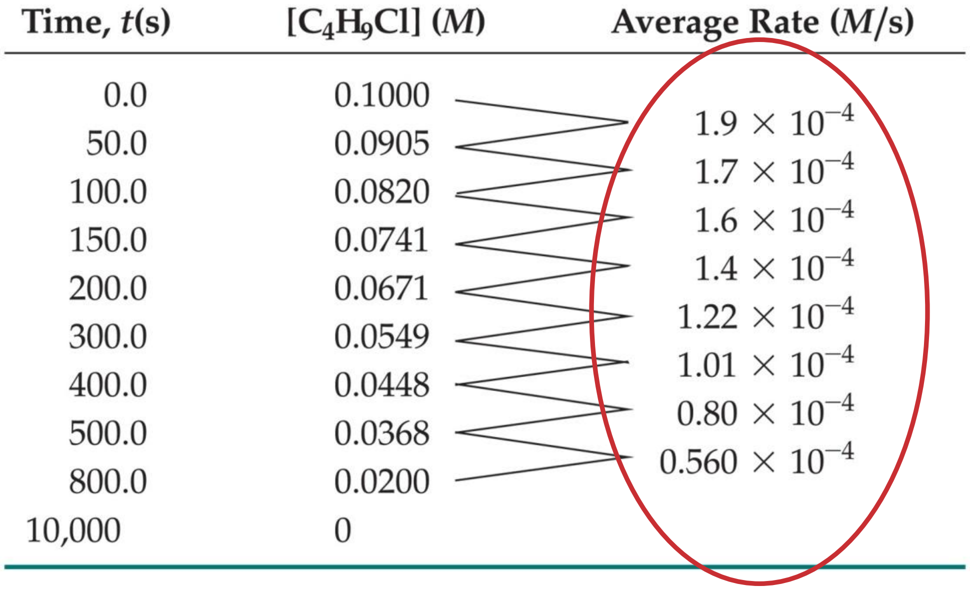
Time, t(s)	$[C_4H_9Cl]$ (M)	Average Rate (M/s)
0.0	0.1000	
		1.9×10^{-4}
50.0	0.0905	
		1.7×10^{-4}
100.0	0.0820	
		1.6×10^{-4}
150.0	0.0741	
		1.4×10^{-4}
200.0	0.0671	
		1.22×10^{-4}
300.0	0.0549	
		1.01×10^{-4}
400.0	0.0448	
		0.80×10^{-4}
500.0	0.0368	
		0.560×10^{-4}
800.0	0.0200	
10,000	0	

The *average rate* of the reaction over each interval is the change in *concentration* divided by the change in *time*:

$$\text{Average rate} = \frac{\Delta[C_4H_9Cl]}{\Delta t}$$

Reaction Rates

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



Time, t(s)	$[C_4H_9Cl]$ (M)	Average Rate (M/s)
0.0	0.1000	1.9×10^{-4}
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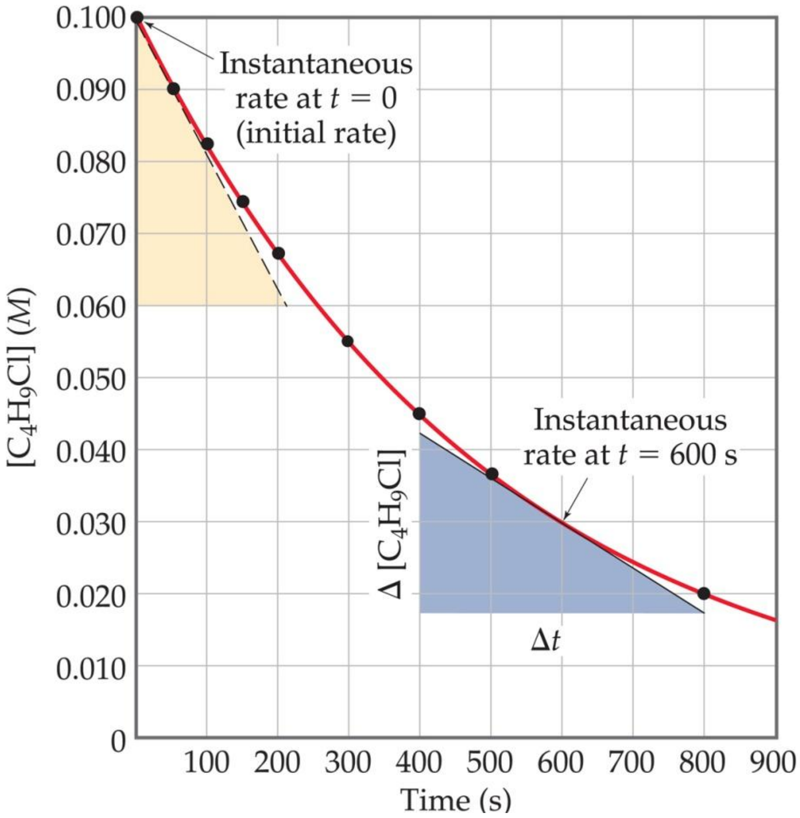
150.0	0.0741	1.4×10^{-4}
200.0	0.0671	1.22×10^{-4}
300.0	0.0549	1.01×10^{-4}
400.0	0.0448	0.80×10^{-4}
500.0	0.0368	0.560×10^{-4}
800.0	0.0200	
10,000	0	

- A plot of *concentration* vs. *time* for this reaction yields a curve like this.
- The slope of a line *tangent* to the *curve* at any point is the *instantaneous rate* at that time.



- All reactions *slow down* over time.
- The best indicator of the *rate of a reaction* is the *beginning*.

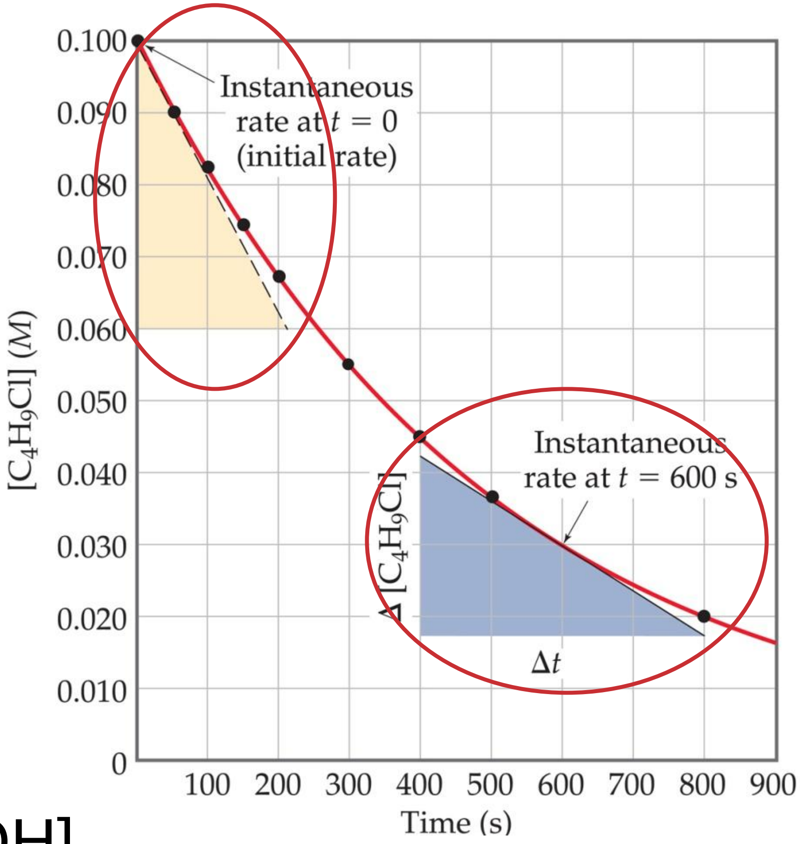
Reaction Rate Changes Over Time

- As time goes on, the rate of a reaction generally slows down
  - because the concentration of the reactants decreases
- At some time the reaction stops, either because the reactants run out or because the system has reached equilibrium

Stoichiometry

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

- In this reaction, the *ratio* of C_4H_9Cl to C_4H_9OH is 1:1
- Thus, the rate of *disappearance* of C_4H_9Cl is the *same* as the rate of *appearance* of C_4H_9OH.



$$\text{Rate} = \frac{-\Delta[C_4H_9Cl]}{\Delta t} = \frac{\Delta[C_4H_9OH]}{\Delta t}$$

Reaction Rates and Stoichiometry

- What if the ratio is *not* 1:1?
- To generalize, then, for the reaction

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

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

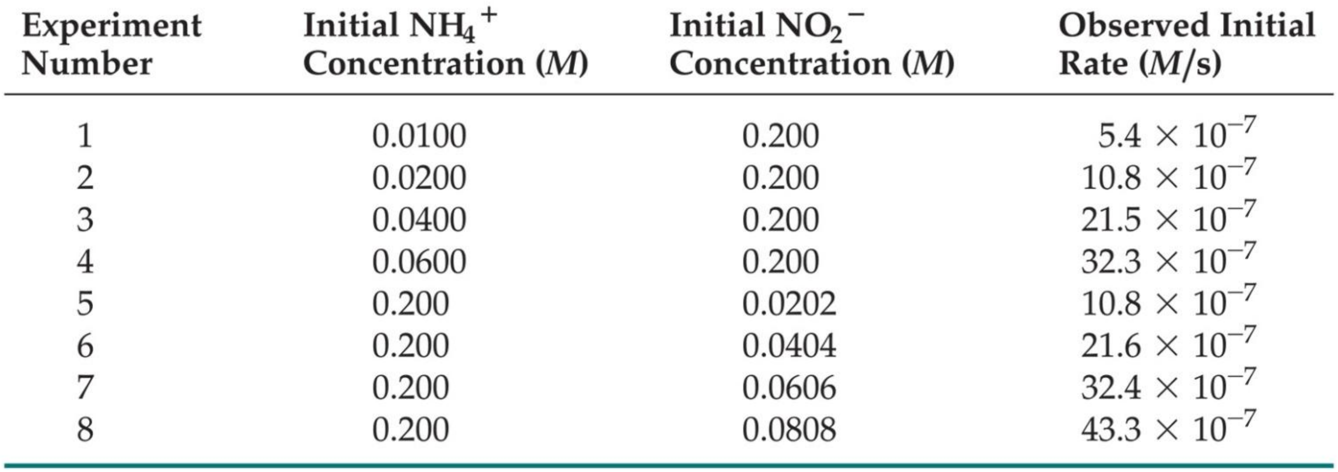
Concentration and Rate

In general rates increase as concentrations increase

$$NH_4^+(aq) + NO_2^-(aq) \rightarrow N_2(g) + 2H_2O(l)$$

- as $[NH_4^+]$ doubles with $[NO_2^-]$ constant the rate doubles,
- as $[NO_2^-]$ doubles with $[NH_4^+]$ constant, the rate doubles,
- We conclude rate $\propto [NH_4^+][NO_2^-]$.

$$\text{Rate} = k[NH_4^+][NO_2^-]$$



Experiment Number	Initial NH_4^+ Concentration (M)	Initial NO_2^- Concentration (M)	Observed Initial Rate (M/s)
1	0.0100	0.200	5.4×10^{-7}
2	0.0200	0.200	10.8×10^{-7}
3	0.0400	0.200	21.5×10^{-7}
4	0.0600	0.200	32.3×10^{-7}
5	0.200	0.0202	10.8×10^{-7}
6	0.200	0.0404	21.6×10^{-7}
7	0.200	0.0606	32.4×10^{-7}
8	0.200	0.0808	43.3×10^{-7}

Rate Laws

- A rate law shows the relationship between the *reaction rate* and the *concentrations* of reactants.
- For a general reaction with rate law

$$\text{Rate} = k[\text{reactant 1}]^{m}[\text{reactant 2}]^{n}$$

reaction is m^{th} order in *reactant 1* and n^{th} order in *react. 2*

- The overall *order* of reaction is $m + n + \ldots$.
- A reaction can be *zero*th order if m, n, … are *zero*.
- Values of the *orders* have to be determined *experimentally*.

Using Initial Rates to Determines Rate Laws

- A reaction is *zero order* in a reactant if the change in *concentration* of that reactant *produces no effect*.
- A reaction is *first order* if *doubling* the *concentration* causes the *rate to double*.
- A reaction is *nth order* if doubling the concentration causes an 2^n *increase* in rate.
- Note that the *rate constant* (k) does *not depend* on *concentration*.

Integrated Rate Laws

Using calculus to integrate the rate law for a *first-order* process gives us

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

Where

$[\mathrm{A}]_0$ is the *initial concentration* of A.

$[\mathrm{A}]_t$ is the *concentration of A* at *some time*, t, during the course of the reaction.

Integrated Rate Laws

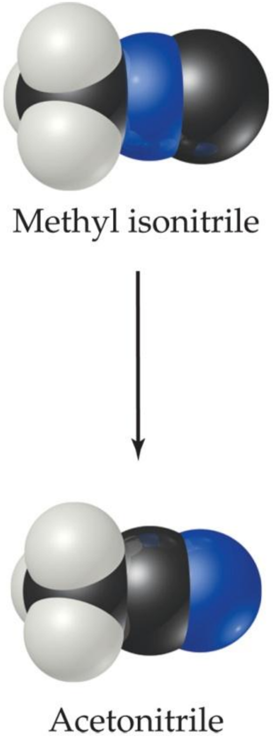
this equation produces…

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

…which is in the form $$y = mx + b$$

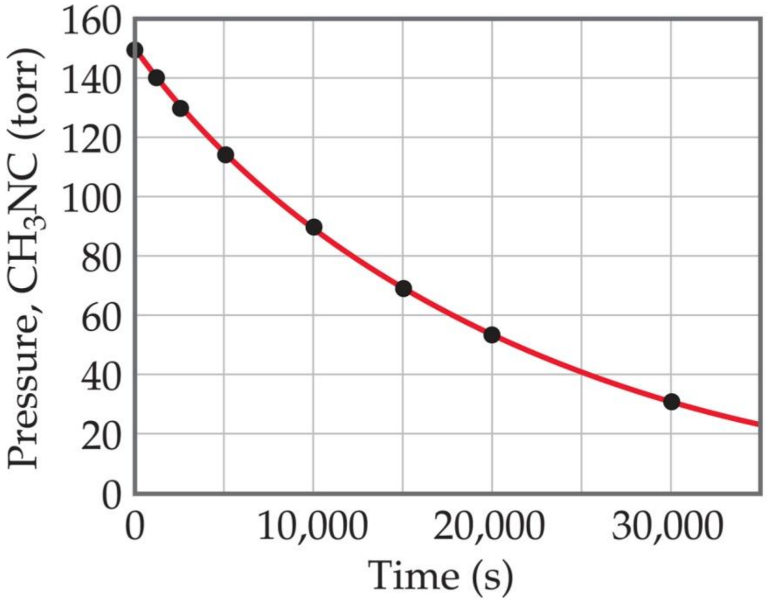
$\ln [A]$ vs. t will yield a *straight line*, and the *slope* of the line will be $-k$.

First-Order Processes



Consider the process in which methyl isonitrile is converted to acetonitrile.

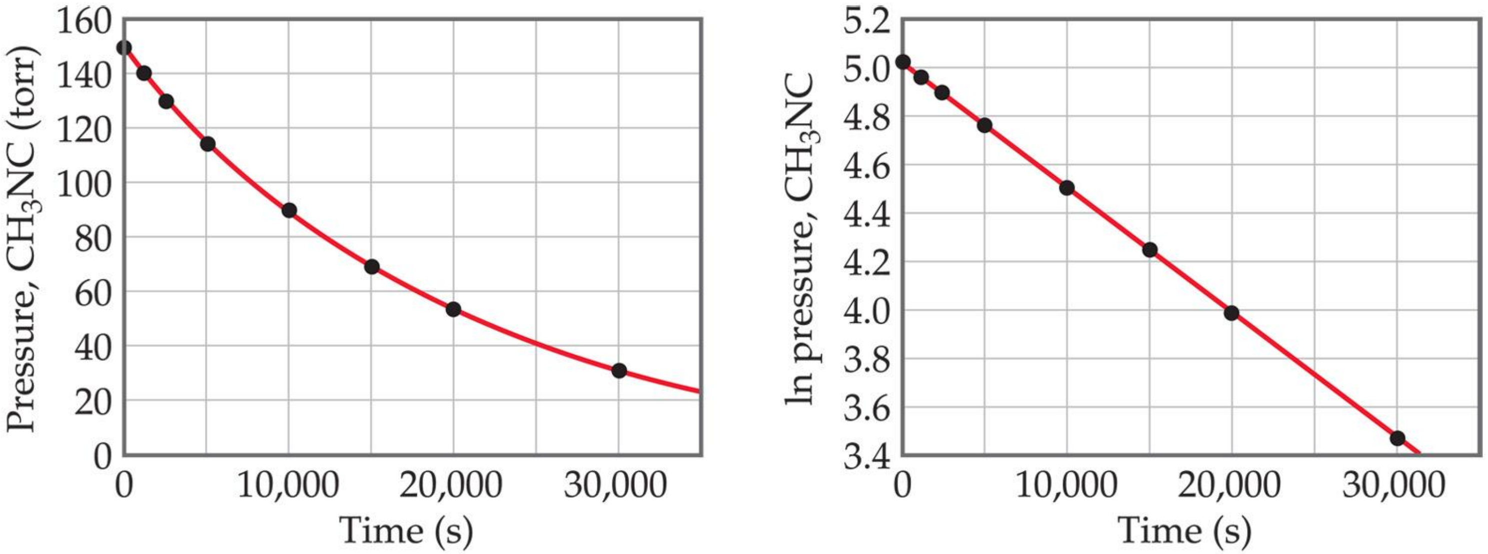
$$CH_3NC \longrightarrow CH_3CN$$



This data was collected for this reaction at 198.9°C

First-Order Processes

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



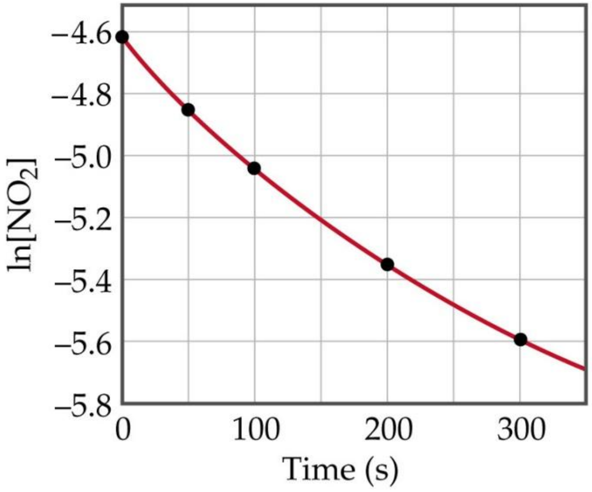
- When ln *P* is plotted as a function of time, a straight line results.
- Therefore,
  - The process is first-order.
  - *k* is the negative slope: $5.1 \times 10^{-5}\ \mathrm{s}^{-1}$.

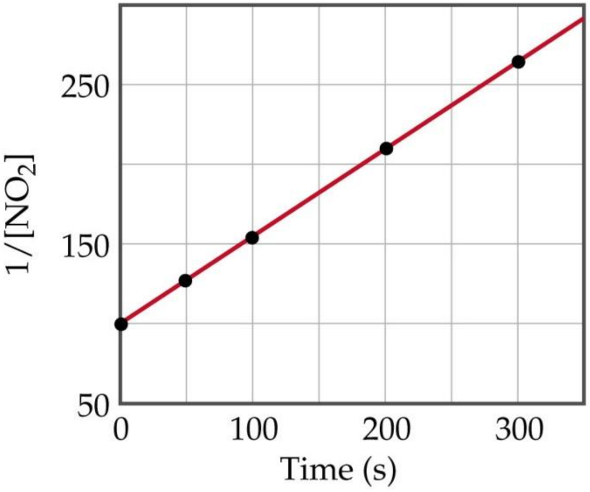
Second-Order Processes

- For a second order reaction with just one reactant

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

- if a process is second-order in A, a plot of 1/[A] vs. *t* will yield a straight line, and the slope of that line is *k*.

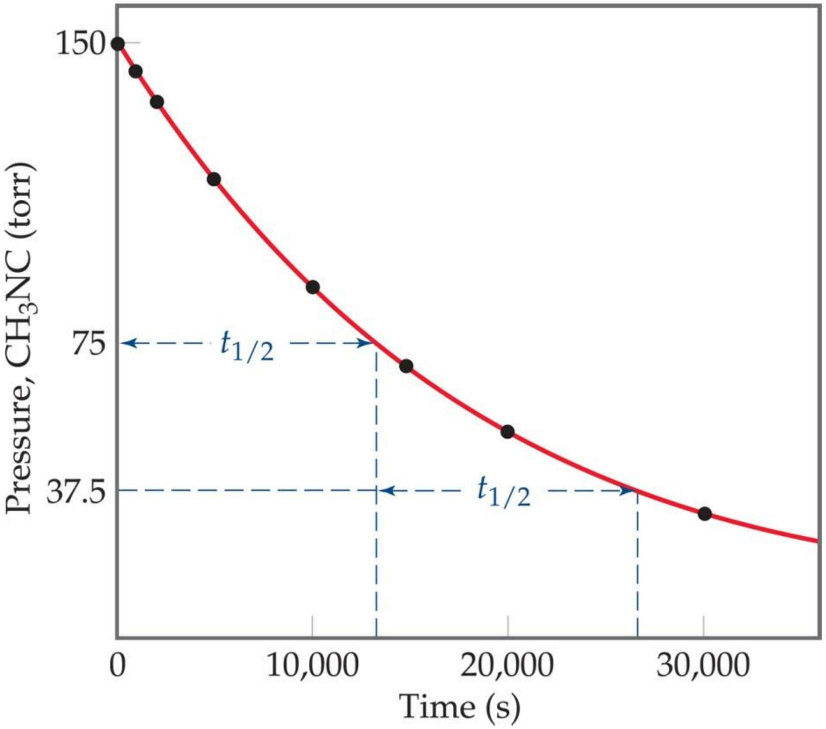




Half-Life

- *Half-life* is the *time* taken for the *concentration* of a reactant to drop to *half* its *original value*.
- For a *first order process*, half life, $t_{1/2}$ is the time taken for $[A]_0$ to reach $\frac{1}{2}[A]_0$.
- Mathematically,

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



Half-Life

- For a second order reaction, half-life depends in the initial concentration:

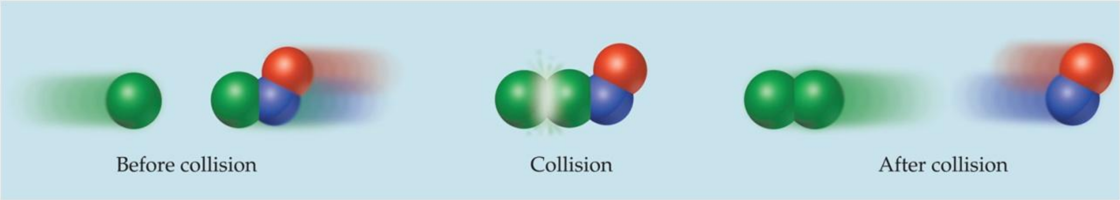
$$\frac{1}{0.5\,[\mathrm{A}]_0} = kt_{1/2} + \frac{1}{[\mathrm{A}]_0}$$

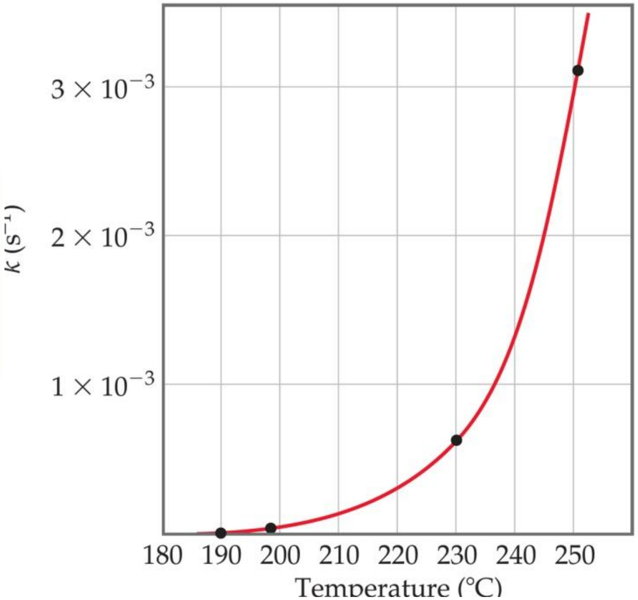
$$\frac{2}{[\mathrm{A}]_0} = kt_{1/2} + \frac{1}{[\mathrm{A}]_0}$$

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

The Collision Model

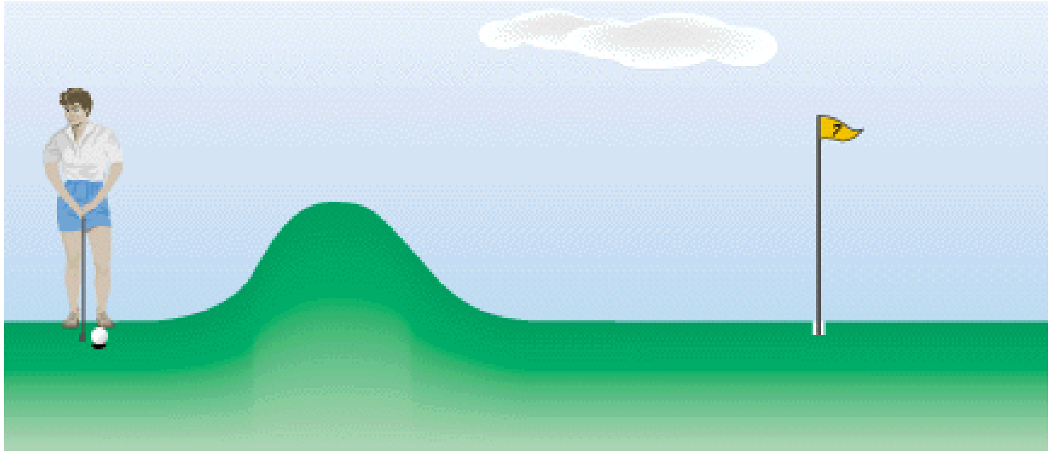
- Generally, as *temperature increases*, so does the *reaction rate*.
- This is because *k is temperature dependent*.
- Molecules can only react
  if they collide with each other.





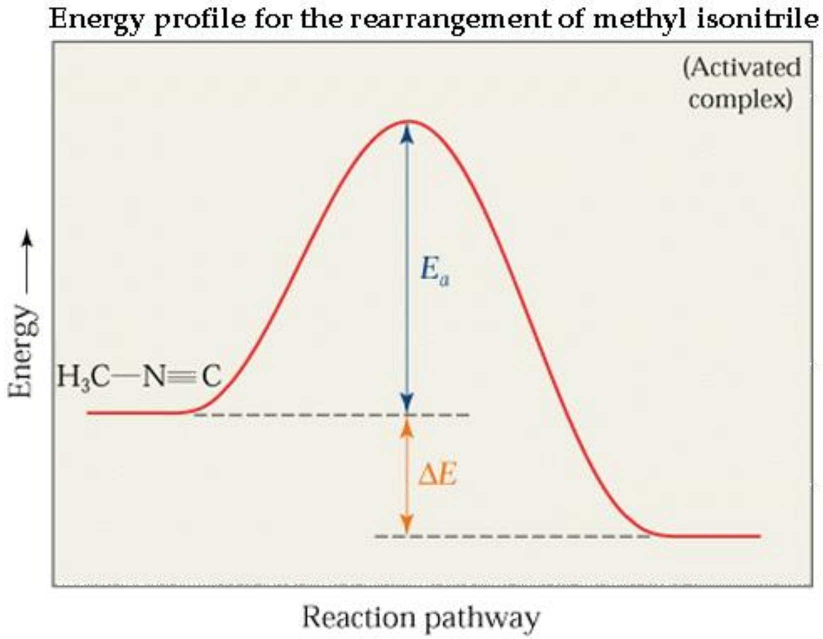
Activation Energy

- minimum energy required to initiate a chemical reaction *activation energy*, E_a.
- Just as a ball *cannot get over* a hill with *enough energy*, a reaction cannot occur unless the molecules possess *sufficient energy* to get over the *activation energy barrier*.



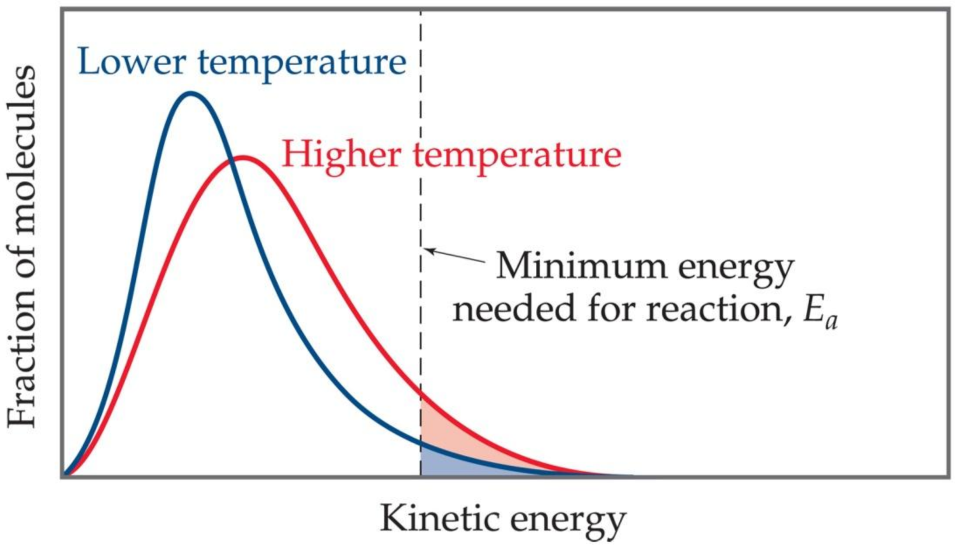
Reaction Coordinate Diagrams

- It *shows* the energy of the *reactants and products* (and, therefore, *ΔE*).
- The high point on the diagram is the transition state.


Energy profile for the rearrangement of methyl isonitrile

- The species present at the transition state is called the activated complex.
- The energy gap between the reactants and the activated complex is the *activation energy barrier*.

Maxwell–Boltzmann Distributions



- At any temperature there is a wide distribution of kinetic energies.
- As the temperature increases, curve flattens and broadens
- Thus at *higher temperatures*, a larger population of molecules has *higher energy*.

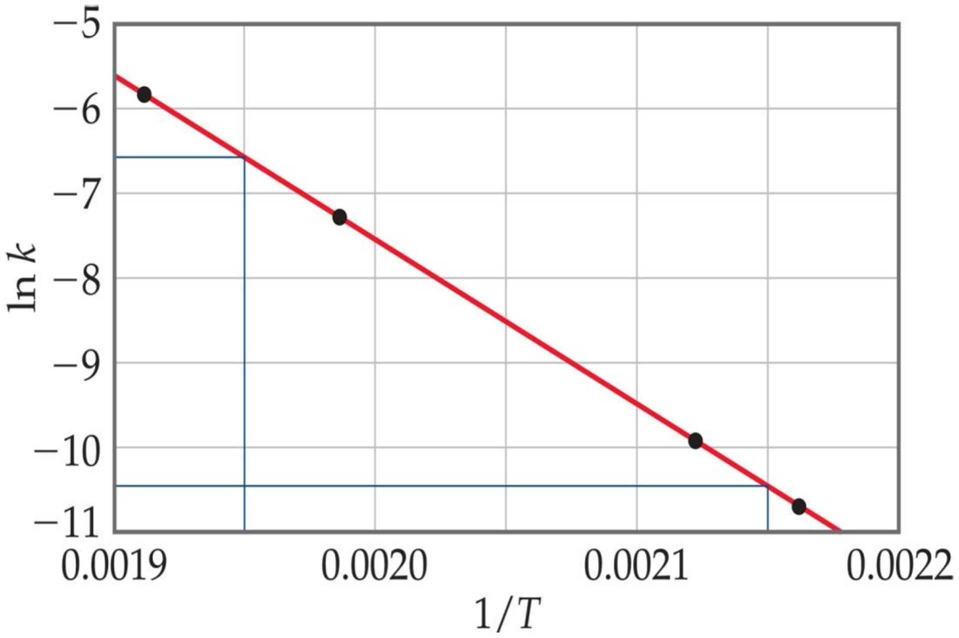
Arrhenius Equation

Svante Arrhenius developed a mathematical relationship between *k* and E_a:

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

where *A* is the frequency factor, a number that represents the *probability* that collisions would occur with the proper orientation for reaction.

Arrhenius Equation



Taking the natural logarithm of both sides, the equation becomes

$$\ln k = -\frac{E_a}{RT} + \ln A$$

$$y \quad = \quad mx + b$$

Therefore, if *k* is determined *experimentally* at several *temperatures*, E_a can be *calculated* from the *slope* of a plot of *ln k* vs. 1/*T*.

Arrhenius Equation

If we do not have a lot of data, then we recognize

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

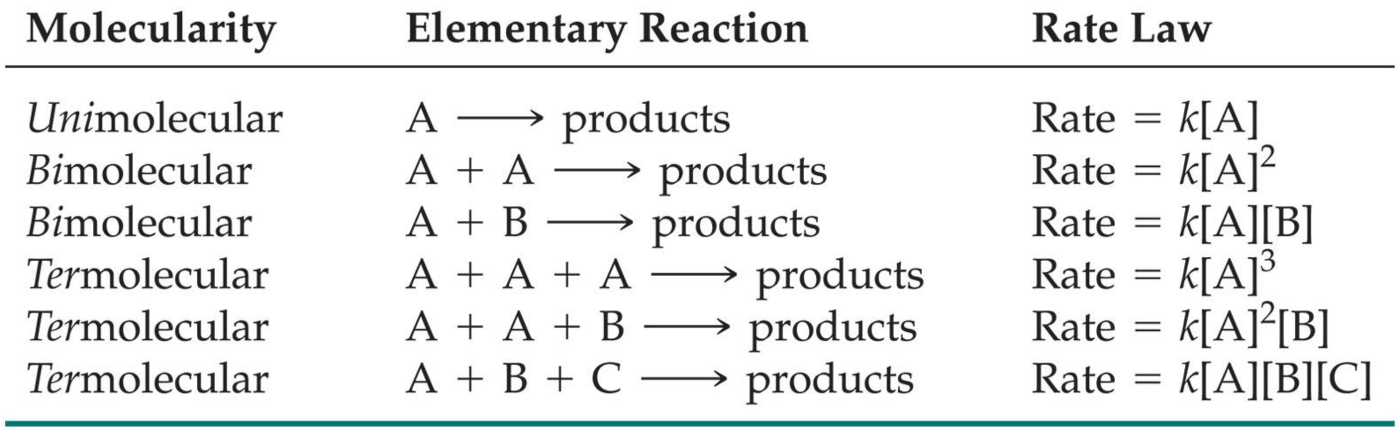
$$\ln k_1 - \ln k_2 = \left(-\frac{E_a}{RT_1} + \ln A\right) - \left(-\frac{E_a}{RT_2} + \ln A\right)$$

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

Reaction Mechanisms

- The balanced *chemical equation* provides information about the *beginning* and *end* of reaction.
- The reaction mechanism gives the *path* of the reaction.
- Reactions may occur all at *once* or through *several* discrete *steps*.
- Elementary step: *any* process that occurs in a *single step*.

Reaction Mechanisms

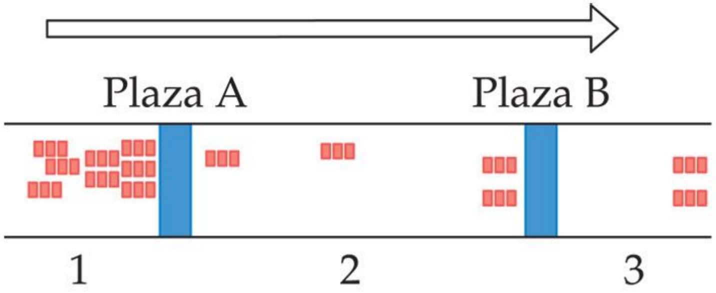


Molecularity	Elementary Reaction	Rate Law
*Uni*molecular	$A \longrightarrow \text{products}$	$\text{Rate} = k[A]$
*Bi*molecular	$A + A \longrightarrow \text{products}$	$\text{Rate} = k[A]^2$
*Bi*molecular	$A + B \longrightarrow \text{products}$	$\text{Rate} = k[A][B]$
*Ter*molecular	$A + A + A \longrightarrow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

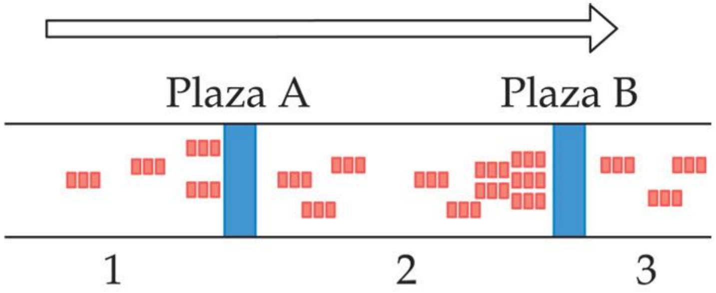
- The molecularity of a process tells how many molecules are involved in the process.
  - Unimolecular: one molecule in the elementary step,
  - Bimolecular: two molecules in the elementary step, and
  - Termolecular: three molecules in the elementary step.

Multistep Mechanisms

- Some reactions proceed through *more* than one *step*
- In a multistep process, one of the steps will be *slower* than all *others*.
- The overall reaction cannot occur faster than this slowest, *rate-determining step*.



Cars slowed at plaza A



Cars slowed at plaza B

Multistep Mechanisms

- Some reaction proceed through more than one step:

$$NO_2(g) + NO_2(g) \rightarrow NO_3(g) + NO(g) \text{ (slow)}$$

$$NO_3(g) + CO(g) \rightarrow NO_2(g) + CO_2(g) \text{ (fast)}$$

- Notice that if we add the above steps, we get the overall reaction:

$$NO_2(g) + CO(g) \rightarrow NO(g) + CO_2(g)$$

- The rate law for this reaction is found experimentally

$$\text{Rate} = k\,[NO_2]^2$$

Fast Initial Step

$$2NO(g) + Br_2(g) \rightarrow 2NOBr(g)$$

- The experimentally determined rate law is

$$\text{Rate} = k[NO]^2[Br_2]$$

- Consider the following mechanism

Step 1: $NO(g) + Br_2(g) \xrightleftharpoons[k_{-1}]{k_1} NOBr_2(g)$ **(fast)**

Step 2: $NOBr_2(g) + NO(g) \xrightarrow{k_2} 2NOBr(g)$ **(slow)**

Fast Initial Step

- The rate law is (based on Step 2):

$$\text{Rate} = k_2[\text{NOBr}_2][\text{NO}]$$

- The rate law should not depend on the concentration of an intermediate (*intermediates are usually unstable*).
- Assume $NOBr_2$ is unstable, so we express the concentration of $NOBr_2$ in terms of NOBr and Br_2 assuming there is an equilibrium in step 1 we have

$$[\text{NOBr}_2] = \frac{k_1}{k_{-1}}[\text{NO}][\text{Br}_2]$$

Fast Initial Step

- By definition of equilibrium:

$$k_1[\mathrm{NO}][\mathrm{Br_2}] = k_{-1}[\mathrm{NOBr_2}]$$

- Therefore, the overall rate law becomes

$$\text{Rate} = k_2 \frac{k_1}{k_{-1}}[\mathrm{NO}][\mathrm{Br_2}][\mathrm{NO}] = k_2 \frac{k_1}{k_{-1}}[\mathrm{NO}]^2[\mathrm{Br_2}]$$

- Note the final rate law is consistent with the experimentally observed rate law.

$$\text{Rate} = \frac{k_2 k_1}{k_{-1}}\ [\mathrm{NO}]\ [\mathrm{Br_2}]\ [\mathrm{NO}] \quad = k\ [\mathrm{NO}]^2\ [\mathrm{Br_2}]$$