Chemical kinetics

Outline

- Reaction rates
- Rate laws
- Integrated rate laws
- Half life
- Arrhenius equation
- Mechanism
- Collision model
- Transition state theory

Kinetics

Å Chemical Kinetics is the study of the rate at which a chemical process occurs.

Å Rate –change in some variable per unit time

$$rate = f\,([A], [B], [Y], [I], [C], T, p, \ldots)$$

Å Reaction rate –change in concentration per unit time; M/s

Kinetics

- **Thermodymanics** - *possibility*
- **Kinetics** – *how fast...*

- Besides information about the speed at which reactions occur, kinetics also sheds light on the reaction mechanism (exactly how the reaction occurs).

- time scale 10^{-15} s – 10^{10} s

  in laboratory 10^{-6} s – 10^{5} s

Reaction rate

A + B → C

$$r_a = -\frac{d[A]}{dt}$$

Rate of disappearence of A

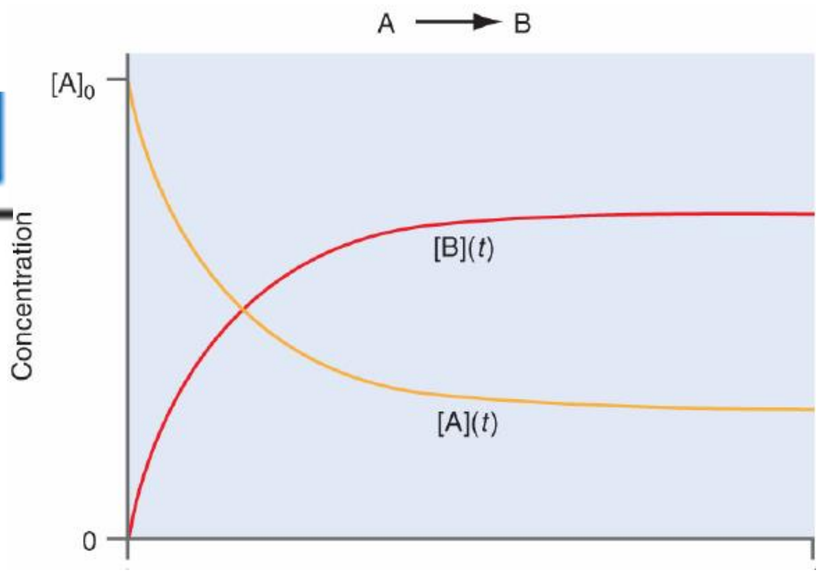
$$r_c = \frac{d[C]}{dt}$$

Rate of appearence of C

Stoichiometry

$$-\frac{d[A]}{dt} = -\frac{d[B]}{dt} = \frac{d[C]}{dt}$$

Rate of reaction



Reaction rate

$2A + B \rightarrow 3C + D$

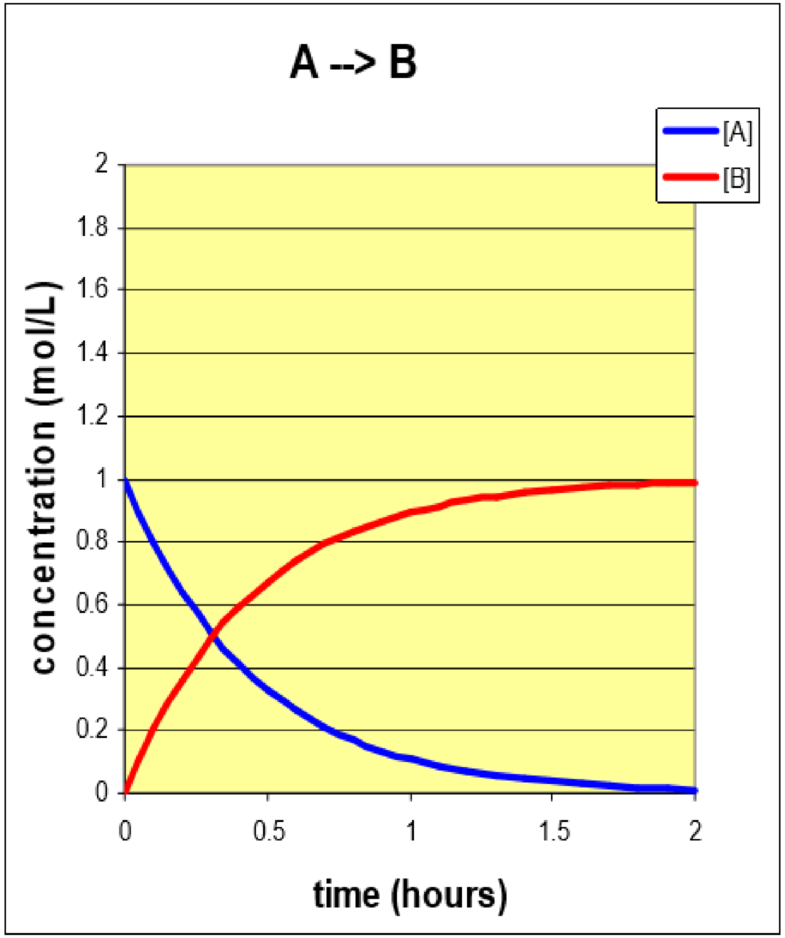
$$-\frac{d[B]}{dt} = -1/2\,\frac{d[A]}{dt} = +1/3\,\frac{d[C]}{dt} = \frac{d[D]}{dt}$$

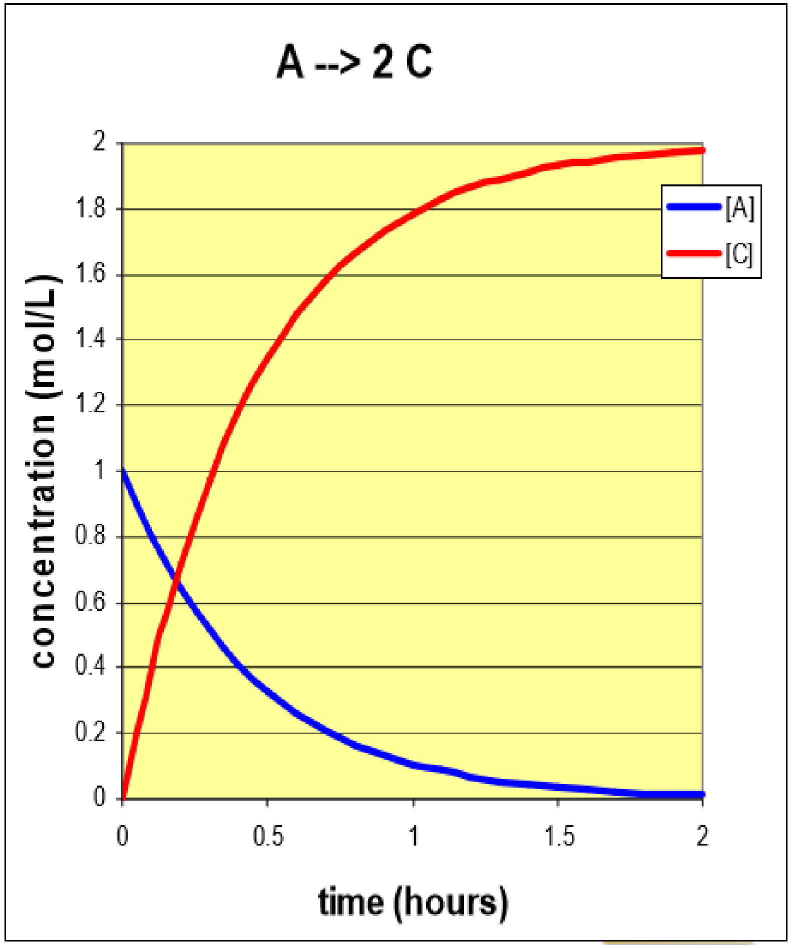
Generally:

$aA + bB \rightarrow cC + dD$

$$-1/a\,\frac{d[A]}{dt} = -1/b\,\frac{d[B]}{dt} = +1/c\,\frac{d[C]}{dt} = +1/d\,\frac{d[D]}{dt}$$

Comparing concentrations of chemicals in a reaction





Types of reaction rate

- Å Instantaneous rate –rate at a specific time
- Å Initial rate –instantaneous rate at t= 0
- Å Average rate –Δ[A] over a specific time interval

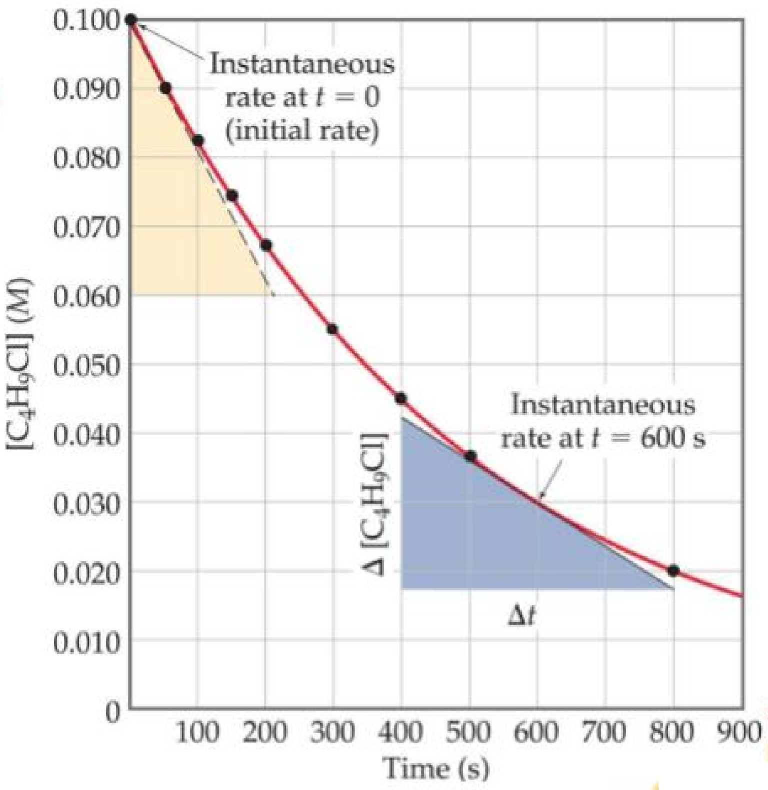
$$\text{Average rate} = \frac{\text{change in number of moles of B}}{\text{change in time}}$$

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

Reaction Rates

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

- 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.



Rate law

Rate Law: equation describing the relationship between the reaction rate and concentration of a reactant or reactants

$$\text{Rate} = k[A]^{\alpha}[B]^{\beta}$$

α – order of reaction with the respect to A

β- order of reaction w.r.t. B

k - rate constant

- Although the exponents in the rate law are often the same as the coefficients in the balanced reaction, this is not necessarily the case.
- Reaction orders and, thus, rate laws must be determined EXPERIMENTALLY!!! they cannot be found by looking at the equation, i.e., the stoichiometry of the reaction

- Overall order = sum of individual order

Reaction order

$$\boxed{2\mathrm{ICl} + \mathrm{H}_2 \longrightarrow \mathrm{I}_2 + 2\mathrm{HCl}}$$

$$\frac{1}{2}\frac{d[\mathrm{HCl}]}{dt} = k[\mathrm{ICl}][\mathrm{H}_2].$$

$$\boxed{2(\mathrm{Mn}^{\mathrm{III}}\mathrm{MG})^{+} + \mathrm{S}_2\mathrm{O}_4^{2-} \longrightarrow 2(\mathrm{Mn}^{\mathrm{II}}\mathrm{MG}) + 2\mathrm{SO}_2,}$$

$$\mathrm{rate} = k[(\mathrm{Mn}^{\mathrm{III}}\mathrm{MG})^{+}][\mathrm{S}_2\mathrm{O}_4^{2-}]^{\frac{1}{2}},$$

Reaction order

Zero order reaction

A→ products

$$-\frac{1}{a}\frac{d[\mathrm{A}]}{dt}=k[\mathrm{A}]^{\circ}$$

First order reaction

$$-\frac{1}{a}\frac{d[\mathrm{A}]}{dt}=k[\mathrm{A}]$$

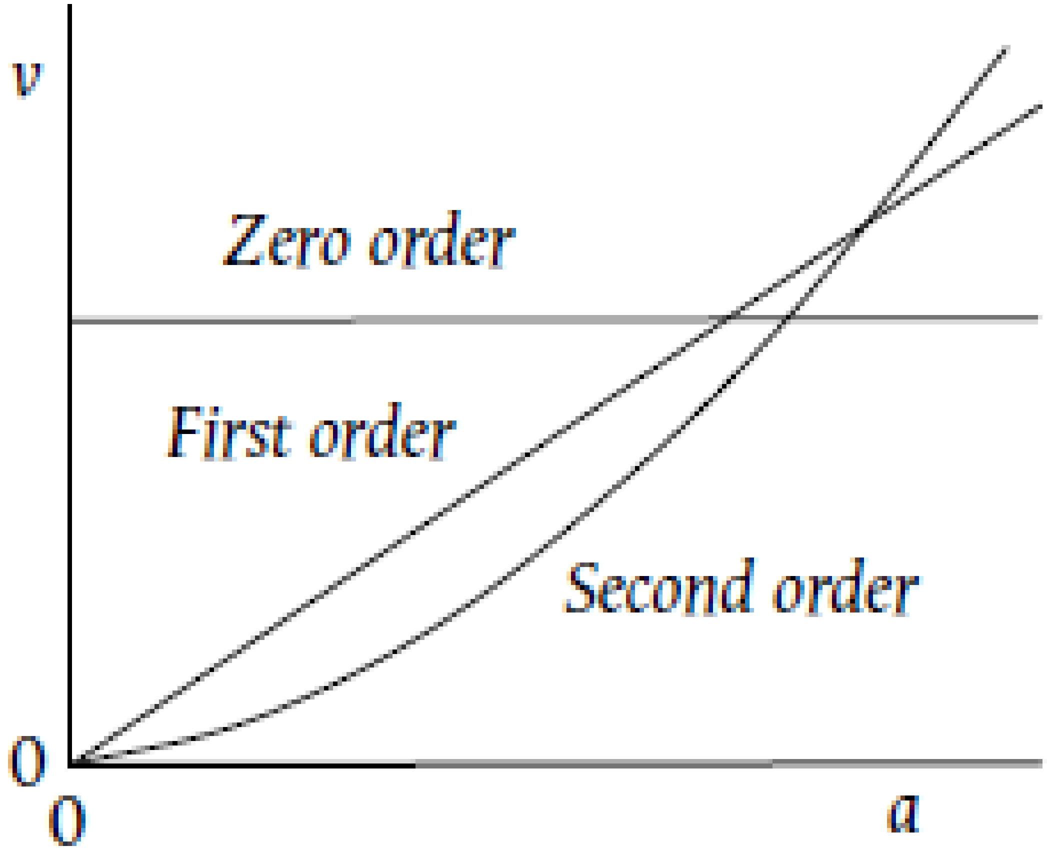
Second order reaction

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

A+B→ products

$$-\frac{1}{a}\frac{d[\mathrm{A}]}{dt}=-\frac{1}{b}\frac{d[\mathrm{B}]}{dt}=k[\mathrm{A}][\mathrm{B}].$$

Reaction order



Factors That Affect Reaction Rates

– Structure, elements, behavior

Basic factors :
- Nature of reactants
- Concentrations of reactants
- Temperature
- Presence of catalysts
- Surface area

Factors That Affect Reaction Rates

Nature of reactants

Å Ions react rapidly:

$Ag^+ + Cl^- \leftrightarrow AgCl(s)$ Very fast

Å Reactions which involve bond breaking are slower:

$NH_4^+ + OCN^- \leftrightarrow OC(NH_2)_2$

Å Redox reactions in solutions are slow

Å Transfer of electrons are faster than those of atoms.

Å Reactions between covalently bonded molecules are slow:

Å $2\,HI(g) \leftrightarrow H_2(g) + I_2(g)$

Factors That Affect Reaction Rates

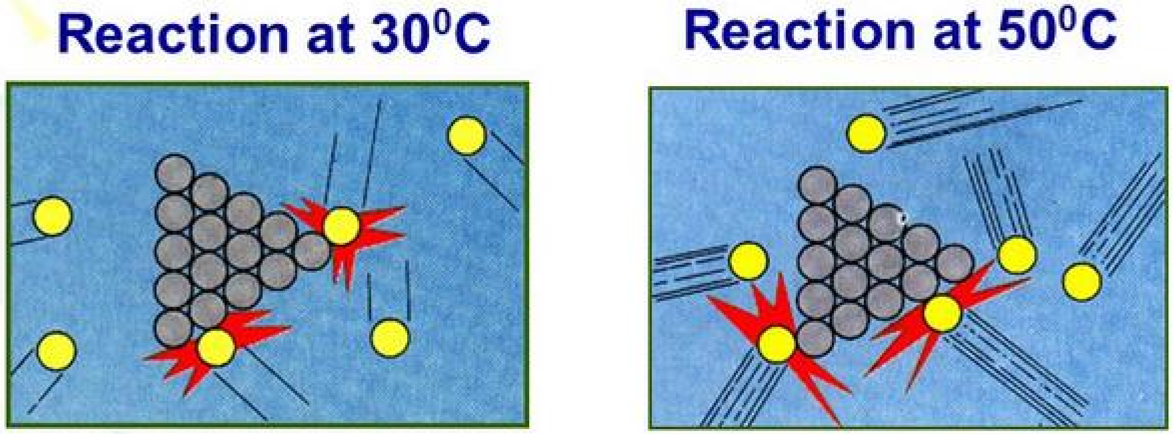
Concentration of Reactants

- As the concentration of reactants increases, so does the likelihood that reactant molecules will collide.

Factors That Affect Reaction Rates

Temperature

- At higher temperatures, reactant molecules have more kinetic energy, move faster, and collide more often and with greater energy



Reaction at 30^0C

Reaction at 50^0C

As the temperature increases the number of collisions increases as well as the energy of the collisions. So temperature has a big effect on the rate of reaction. For every 10^0C increase the rate approximately doubles.

Factors That Affect Reaction Rates

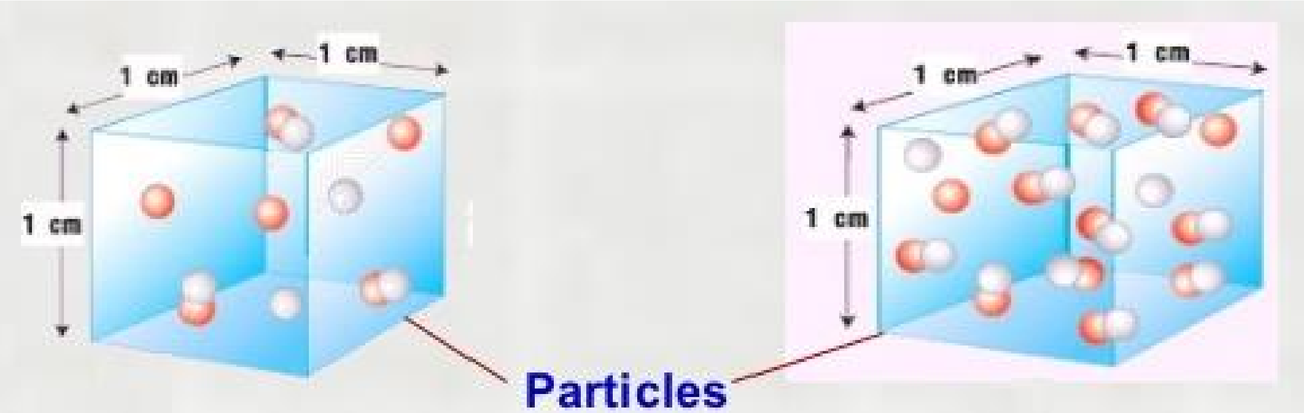
Presence of a Catalyst

- Catalysts speed up reactions by changing the mechanism of the reaction.
- Catalysts are not consumed during the course of the reaction.

Factors That Affect Reaction Rates

Surface Area

Å The rate of reacton increae when the size of the particles is smaller → The total surface area that is exposed to collision between particles are larger → The collision frequency will increase →The rate of reaction also increases



Rate theory

The Arrhenius Equation

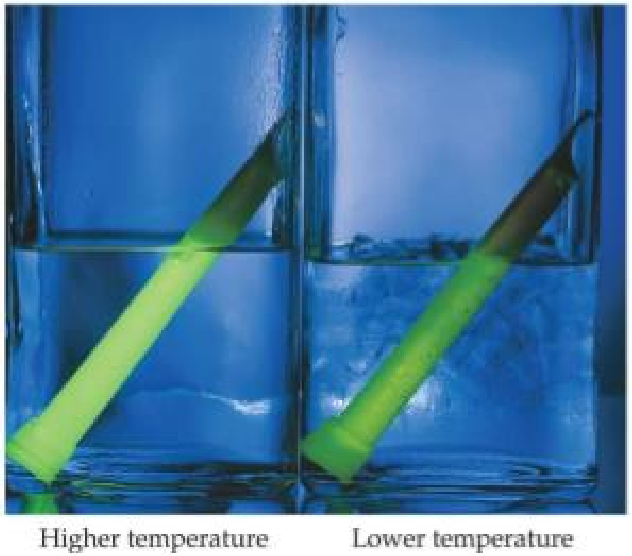
Temperature dependence of the Rate Constant

Most reactions speed up as temperature increases.
(example: food spoils when not refrigerated.)

$$k = f(T)$$

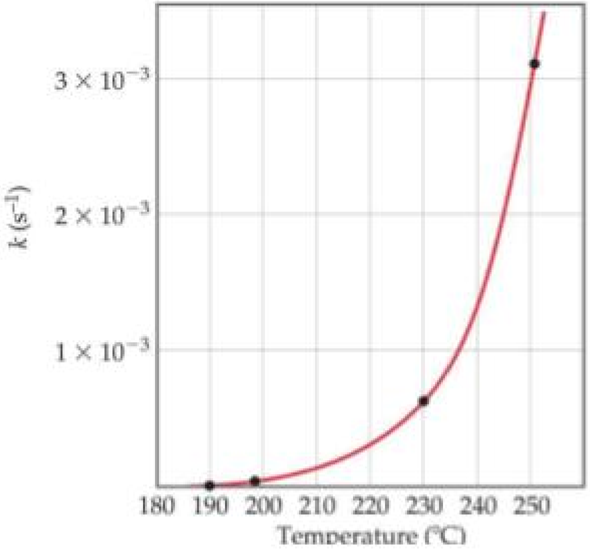
Where “f” is some function.

Temperature and rate


Higher temperature Lower temperature

Generally, as temperature increases, so does the reaction rate.

This is because *k* is temperature dependent.



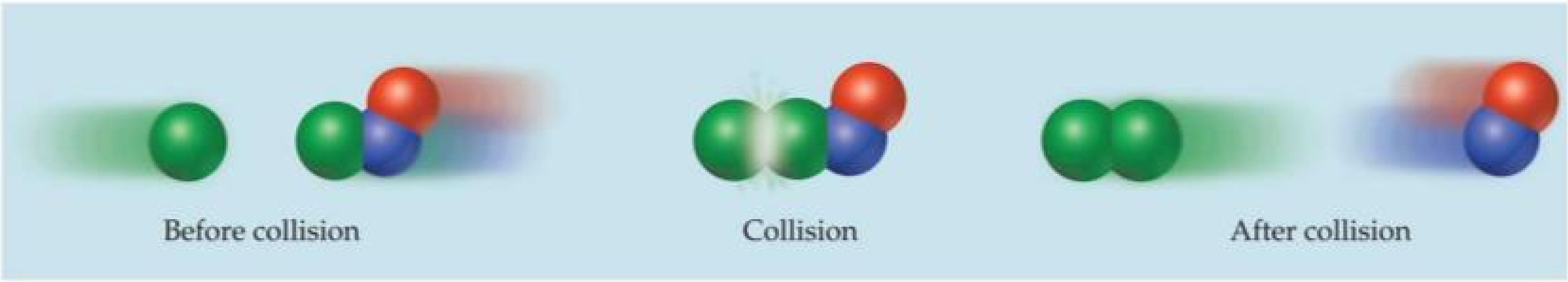
The magnitude of a first order rate constant is seen to increase exponentially with an increase in temperature.

Therefore one can conclude that:

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

The Collision Model

- In a chemical reaction, bonds are broken and new bonds are formed.
- Molecules can only react if they collide with each other
- Furthermore, molecules must collide with the correct orientation and with enough energy to cause bond breakage and formation.

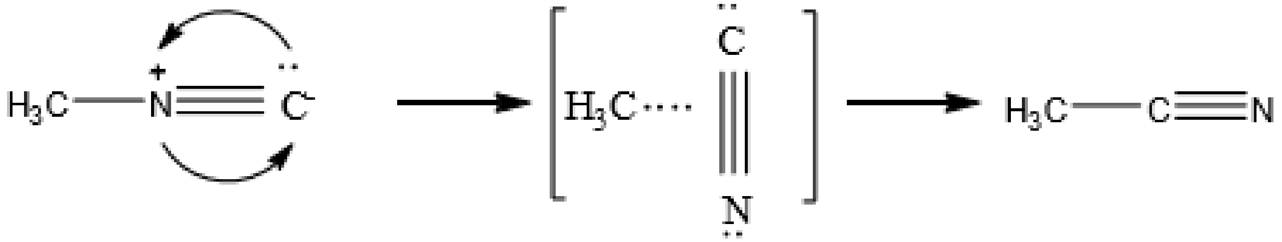


Activation Energy

- In other words, there is a minimum amount of energy required for reaction: the activation energy, Ea

- Just as a ball cannot get over a hill if it does not roll up the hill with enough energy, a reaction cannot occur unless the molecules possess sufficient energy to get over the activation energy barrier.

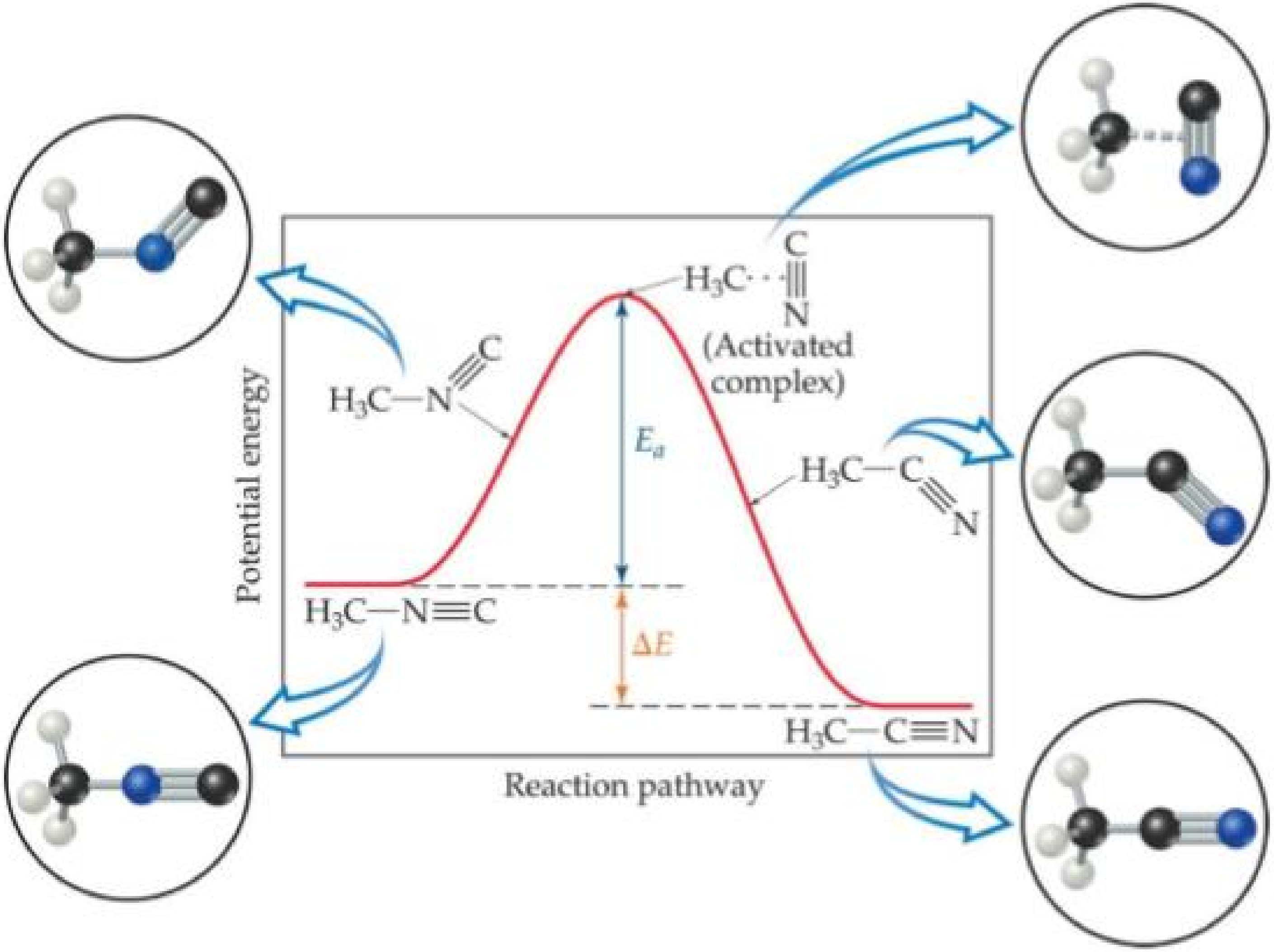
Transition State Theory



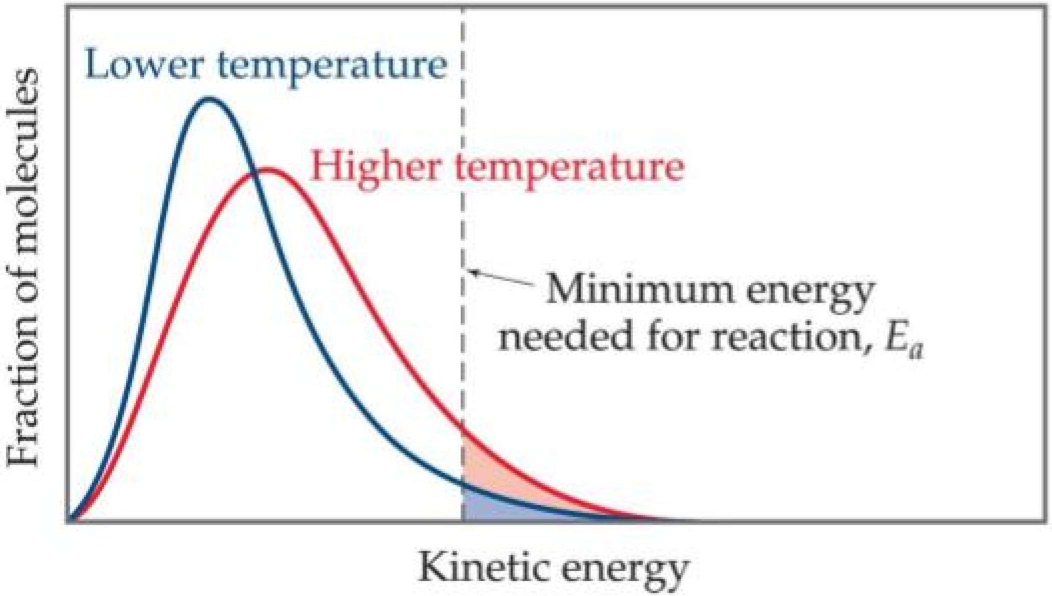
Å This is a reaction where methyl isonitrileis rearranging to acetonitrile

Å This reaction passes through an intermediate state in which the $N\equiv C$ is sitting sideways.

Reaction Coordinate Diagram



Maxwell – Boltzmann distribution



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

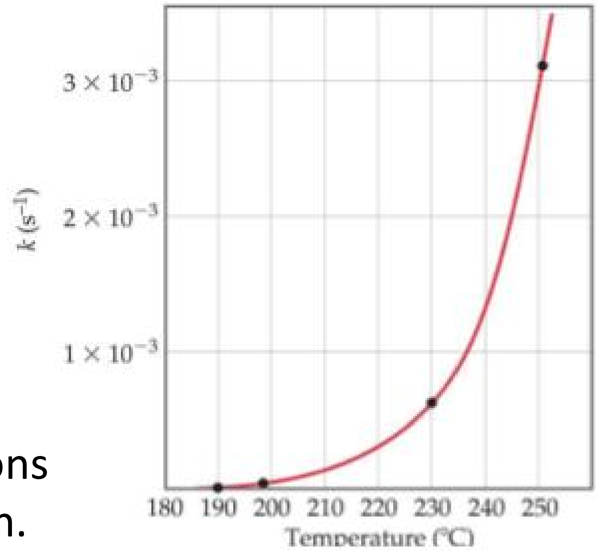
Å As the temperature increases, the curve flattens and broadens.

Å Thus at higher temperatures, a larger population of molecules has higher energy

Arrhenius Equation

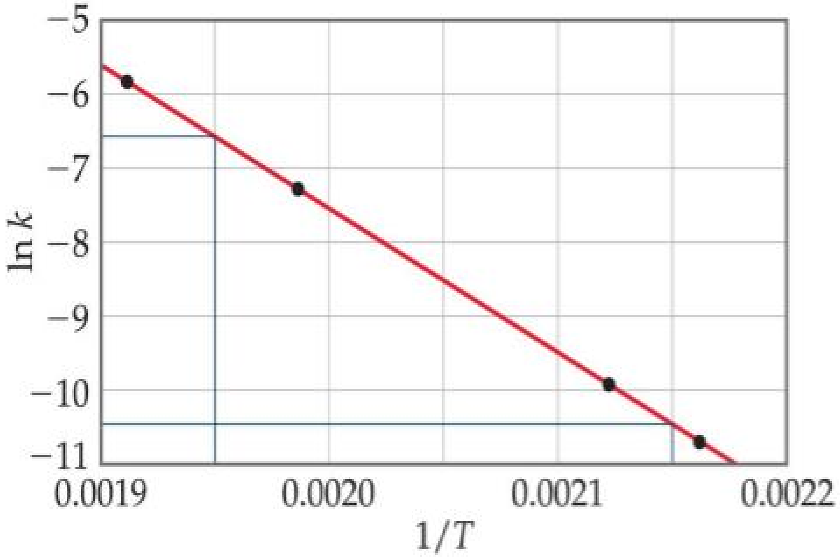
- Fraction of molecules possessing Ea or greater
- number of collisions per second
- fraction of molecules having the correct orientation

$$k = A\,e^{-E_a/RT}$$



A - frequency factor
- a number that represents the likelihood that collisions would occur with the proper orientation for reaction.

Arrhenius Equation



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

$$y = mx + b$$

Arrhenius Equation

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

$$\ln k_1 - \ln k_2 = [\,-Ea/RT_1 + \ln A] - [\,-Ea/RT_2 + \ln A]$$

$$\ln k_1/k_2 = \frac{Ea}{R}\,(1/T1-1/T2)$$

$$\ln k_1 = \frac{Ea}{R}\,(1/T_2 \; -1/T_1)$$