GENERAL CHEMISTRY

Chapter 5
Chemical Kinetics

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Kinetics

- Kinetics is the study of how fast chemical reactions occur: rxn rate

- There are 4 important factors which affect the rates of chemical reactions:

  - **reactant concentration,**

  - **temperature,**

  - action of catalysts, and

  - surface area.

- Reaction mechanism (rxn pathway)

Reaction Rates

- The speed of a reaction is defined as the change that occurs per unit time per unit volume.

  - It is determined by measuring the change in concentration of a reactant or product with time.

  - The speed of the reaction is called the **reaction rate**.

- For a reaction A → B

$$\text{Average rate} = \frac{1}{Volume} \frac{\text{change in number of moles of B}}{\text{change in time}}$$

$$= \frac{\Delta(\text{moles of B})}{V\Delta t} = \frac{\Delta(\text{concentration of B})}{\Delta t} = \frac{\Delta C_B}{\Delta t}$$
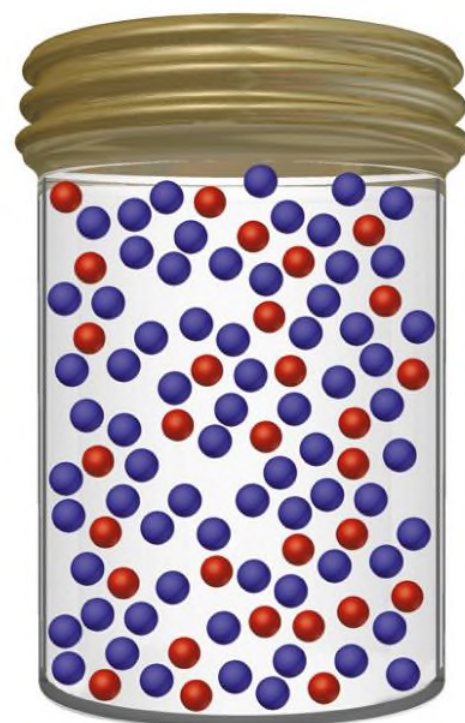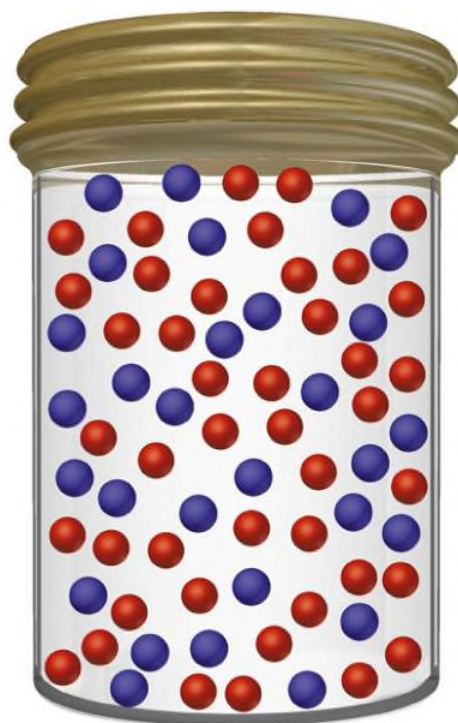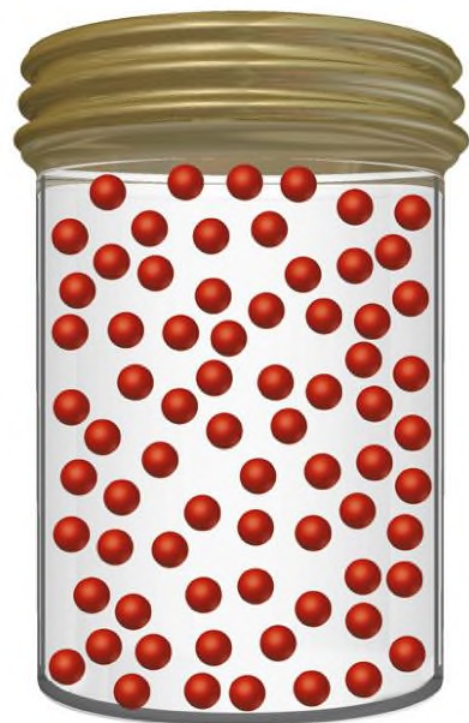
- Suppose A reacts to form B. Let us begin with 1.00 mol A in 1 L-container.

Change in Concentration of Reactions

Calculating Reaction Rates Using Products

– At $t = 0$ (time zero) there is 1.00 mol A (100 red spheres) and no B present.

– At $t = 10$ min, there is 0.54 mol A and 0.46 mol B.

– At $t = 20$ min, there is 0.30 mol A and 0.70 mol B.

– Calculating,

$$\textbf{Average rate} = \frac{\Delta\left(\textbf{moles of B}\right)}{V \Delta t}$$

$$= \frac{\left(\textbf{moles of B at } t = 10\right) - \left(\textbf{moles of B at } t = 0\right)}{1 \times \left(10\ \textbf{min} - 0\ \textbf{min}\right)}$$

$$= \frac{0.46\ \textbf{mol} -\ \textbf{0 mol}}{1 \times \left(10\ \textbf{min} - 0\ \textbf{min}\right)} = 0.046\ \textbf{mol/L.min}$$

Calculating Reaction Rates Using Reactants

- For the reaction A $\rightarrow$ B there are two ways of measuring rate:
  - the speed at which the products appear (i.e. change in moles of B per unit time), or
  - the speed at which the reactants disappear (i.e. the change in moles of A per unit time).

$$\text{Average rate with respect to A} = -\frac{\Delta(\text{moles of A})}{V\,\Delta t} = -\frac{\Delta C_A}{\Delta t}$$

  - The equation, when calculating rates of reactants, is multiplied by -1 to compensate for the negative concentration change.
    - By convention rates are expressed as positive numbers.

Reaction Rates

- Most useful units for rates are to look at molarity (mole/L or M). Since volume is constant, molarity and moles are directly proportional.

- Consider:

  - $C_4H_9Cl(aq) + H_2O(l) \rightarrow C_4H_9OH(aq) + HCl(aq)$
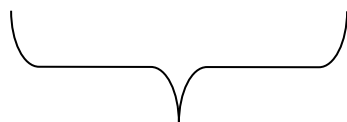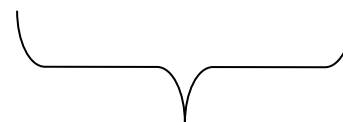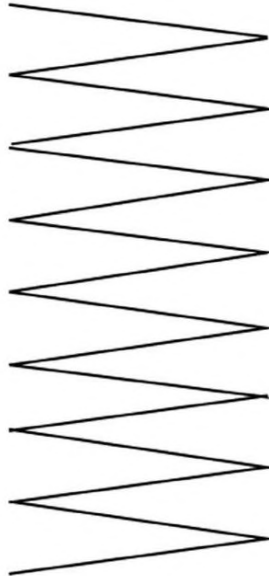
Reactants   Products

Reaction Rates for C$_4$H$_9$Cl

TABLE 14.1	Rate Data for Reaction of C$_4$H$_9$Cl with Water	
Time, t (s)	[C$_4$H$_9$Cl] (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	

Properties of C$_4$H$_9$Cl Reaction

- C$_4$H$_9$Cl(*aq*) + H$_2$O(*l*) $\rightarrow$ C$_4$H$_9$OH(*aq*) + HCl(*aq*)
  - We can calculate the average rate in terms of the disappearance of C$_4$H$_9$Cl.
  - The units for average rate are mol/L·s or *M/s*.
  - The average rate decreases with time.
  - We plot [C$_4$H$_9$Cl] versus time.
  - The rate at any instant in time (instantaneous rate) is the slope of the tangent to the curve.
  - Instantaneous rate is different from average rate.
  - We usually call the instantaneous rate the rate.

Calculating Reaction Rates Using Reactants

$$\text{Average rate with respect to A} = -\frac{\Delta\left(\text{moles of A}\right)}{V\,\Delta t}$$

$$\text{Instantaneous rate with respect to A} = \lim_{\Delta t \to 0} -\frac{\Delta C_A}{\Delta t} = -\frac{dC_A}{dt}$$

Instantaneous Reaction Rates for C₄H₉Cl
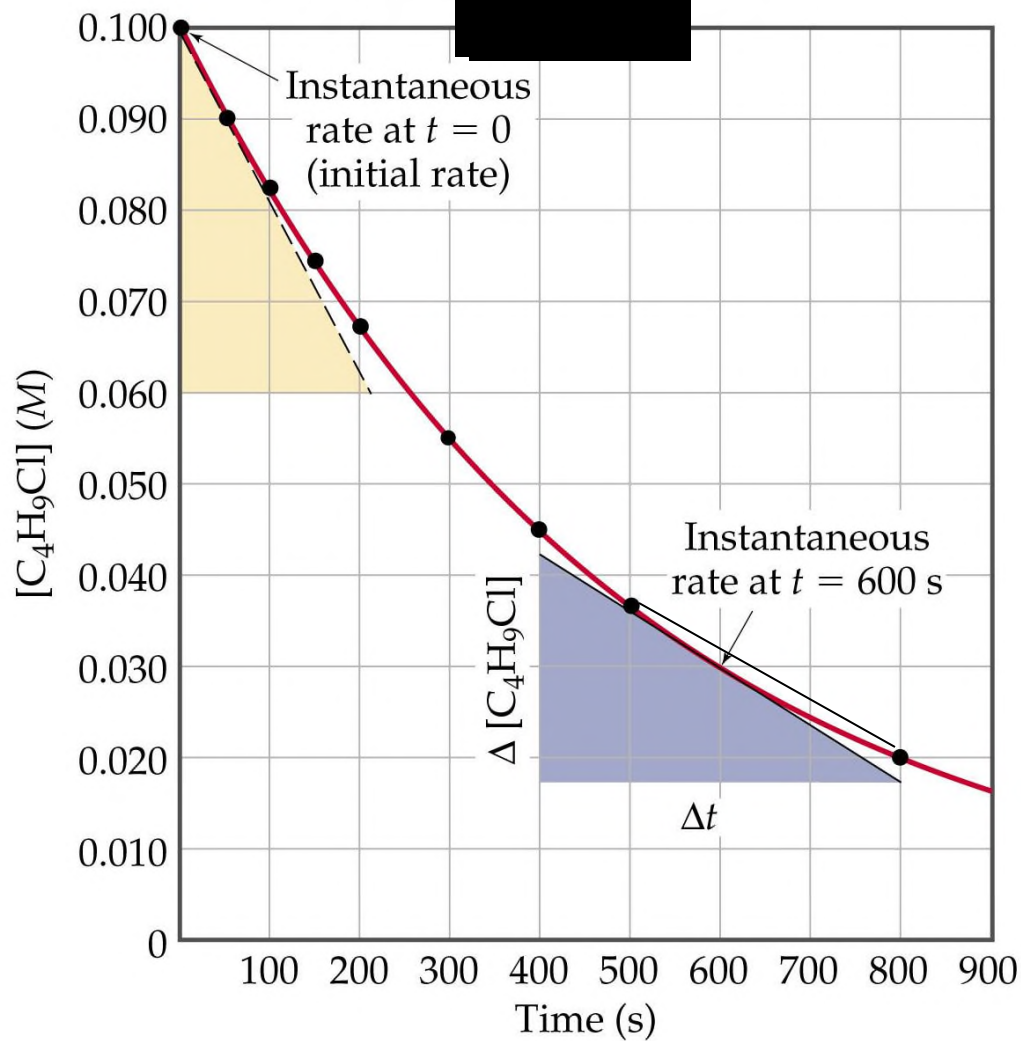
Reaction Rates and Stoichiometry

- For the reaction

$$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$$

we know

1 mole of N2 disappeared   3 mole of H2 disappear

2 mole of NH3 appeared

- Rate(H2) = 3 times the rate(N2)

- Rate(NH3)=2 times the rate(N2)

- $\dfrac{rate_{N2}}{1} = \dfrac{rate_{H2}}{3} = \dfrac{rate_{NH3}}{2}$

Reaction Rates and Stoichiometry

- In general for

$$a\text{A} + b\text{B} \rightarrow c\text{C} + d\text{D}$$

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

Concentration and Rate Table

- In general rates increase as concentrations increase.

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

TABLE 14.2	Rate Data for the Reaction of Ammonium and Nitrite Ions in Water at 25°C		
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}

Concentration and Rate Equation

- For the reaction

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

we note
  - 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 $\propto [NH_4^+][NO_2^-]$.

- Rate law:

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

- The constant k is the rate constant.

Exponents in the Rate Law

- For a general reaction with rate law

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

  we say the reaction is mth order in reactant 1 and nth order in reactant 2.

- The overall order of reaction is $m + n + \ldots$

- A reaction can be zeroth order if $m, n, \ldots$ are zero.

- Note the values of the exponents (orders) have to be determined experimentally. They are not simply related to stoichiometry.

- k is rate constant, independent on concentration.

- rate=k when [reactant 1]=[reactant 2]=..=1 M

- k is specific rate

Determining Order of Reactions

- A reaction is zero order in a reactant if the change in concentration of that reactant produces no effect.

- A reaction is first order in a reactant if doubling the concentration of that reactant causes the rate to double.

- A reaction is nth order in a reactant if doubling the concentration of that reactant causes an 2^n increase in rate.

- Note that the rate constant does not depend on concentration.

Experiment Number	[A] (M)	[B] (M)	Initial Rate (M/s)
1	0.273	0.763	2.83
2	0.273	1.526	2.83
3	0.819	0.763	25.47

Temperature and Rate

The Collision Model

- Most reactions speed up as temperature increases. (E.g. food spoils when not refrigerated.)

- When two light sticks are placed in water: one at room temperature and one in ice, the one at room temperature is brighter than the one in ice.

- The chemical reaction responsible for chemiluminescence is dependent on temperature: the higher the temperature, the faster the reaction and the brighter the light.

The Collision Model
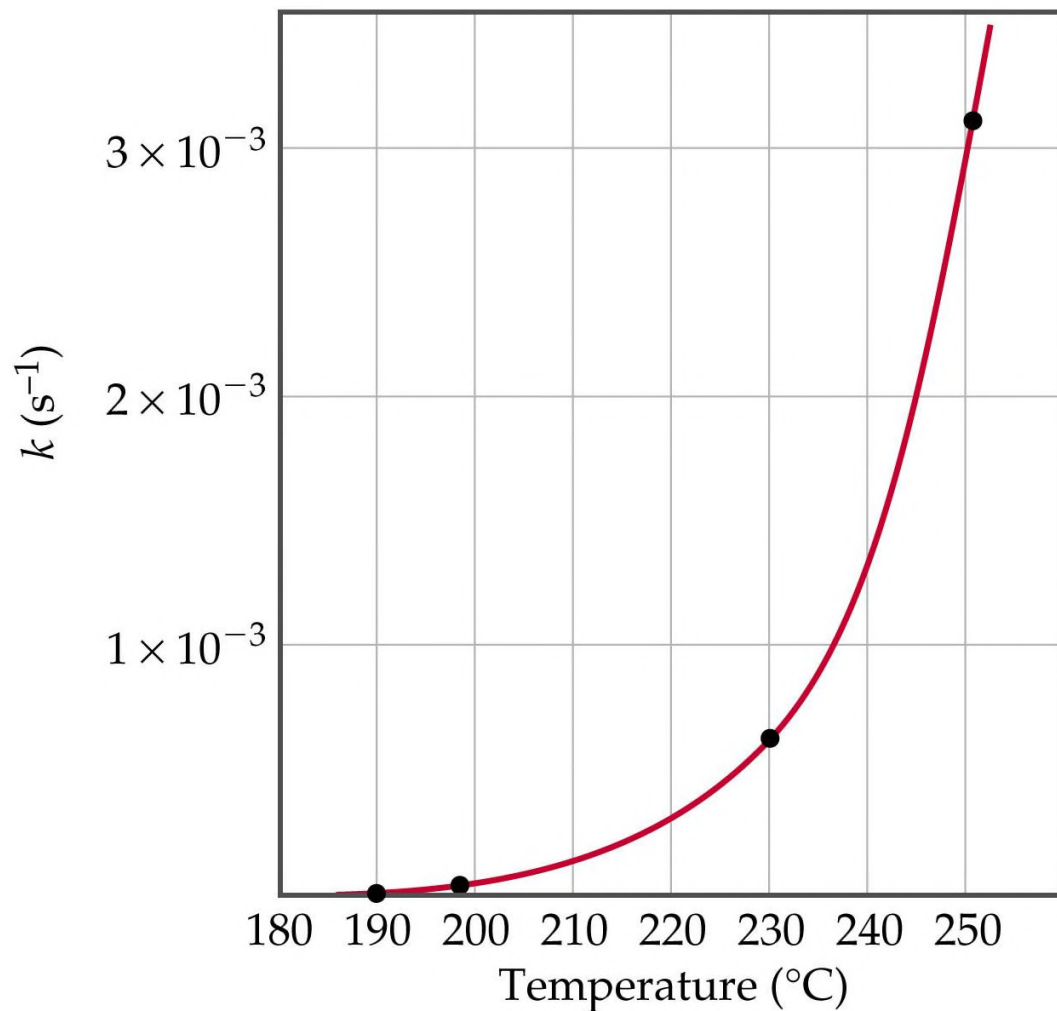
- As temperature increases, the rate increases (very fast).

Q10 rule

- Reaction rate increases very fast with an increase in temperature

- Q10 Rule: temperature increases 10 ^{o}C, rate increases Q10 times (2<Q10<4)

- γ times (van Hoff temperature factor)

- temperature increase n*10 ^{o}C, rate increases: γ^n times

Collision Model: The Central Idea

- Goal: develop a model that explains why rates of reactions increase as concentration and temperature increases.

- The collision model: in order for molecules to react they must collide. A + B → P : A and B must collide

- The greater the number of collisions the faster the rate.

- The more molecules present, the greater the probability of collision and the faster the rate.

- Faster moving molecule collide with greater energy and more frequently, increasing reaction rates.

Collision Model

- Effect of concentration: more molecules present in a unit volume → more chance to collide → faster the rate

- C increases → rate increases

- T increases → molecules move faster → more chance to collide → faster the rate: not enough

- T=298 to 308: average speed increase <3% (10/300), velocity of molecules increase very little (not significant)

- However, rate increases at least 2 times

- Further develop the model, not just use the simple collision

The Speed of a Reaction

The Collision Model

- The higher the temperature, the more energy available to the molecules and the faster the rate.

- Complication: **not all collisions lead to products**. In fact, only a small fraction of collisions lead to product.
 - Why is this?

The Orientation Factor

- In order for reaction to occur the reactant molecules must collide in the correct orientation and with enough energy to form products.
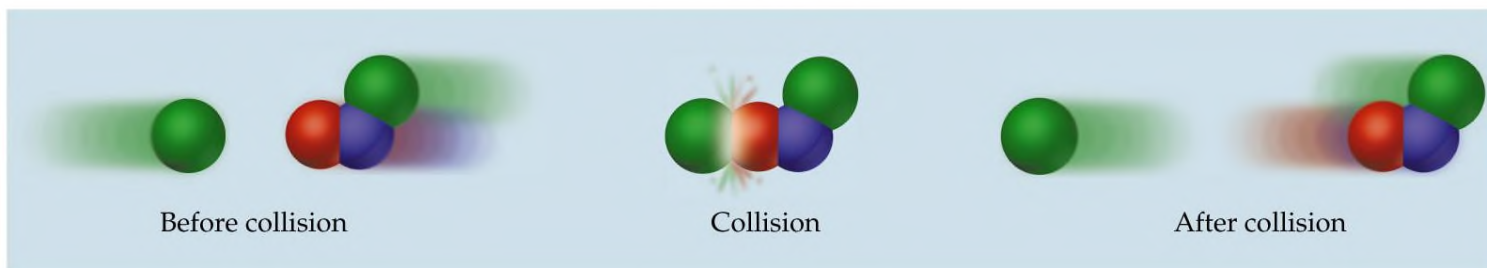
The Orientation Factor

- Consider:

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

- There are two possible ways that Cl atoms and NOCl molecules can collide; one is effective and one is not.

Before collision   Collision   After collision

(a) Effective collision
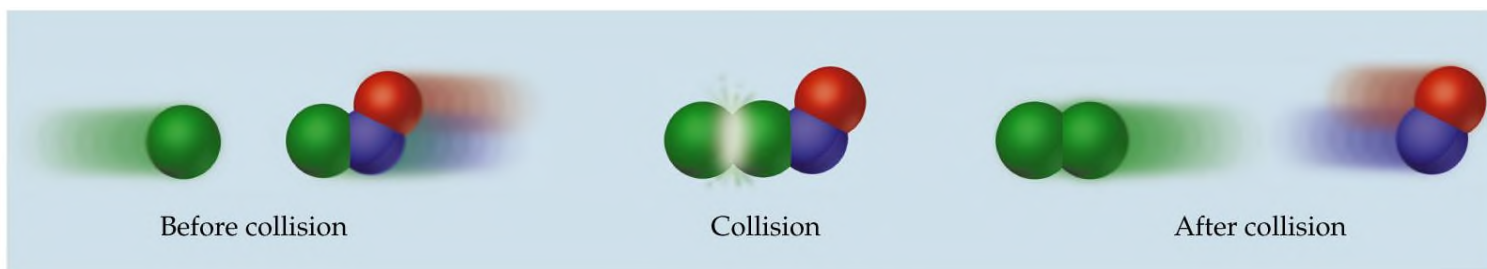
Before collision   Collision   After collision

(b) Ineffective collision

Activation Energy

- Arrhenius: molecules must posses a minimum amount of energy to react. Why?
  - In order to form products, bonds must be broken in the reactants.
  - Bond breakage requires energy.
- Activation energy, E_a, is the minimum energy required to initiate a chemical reaction.

Energy Profile for Methyl Isonitrile
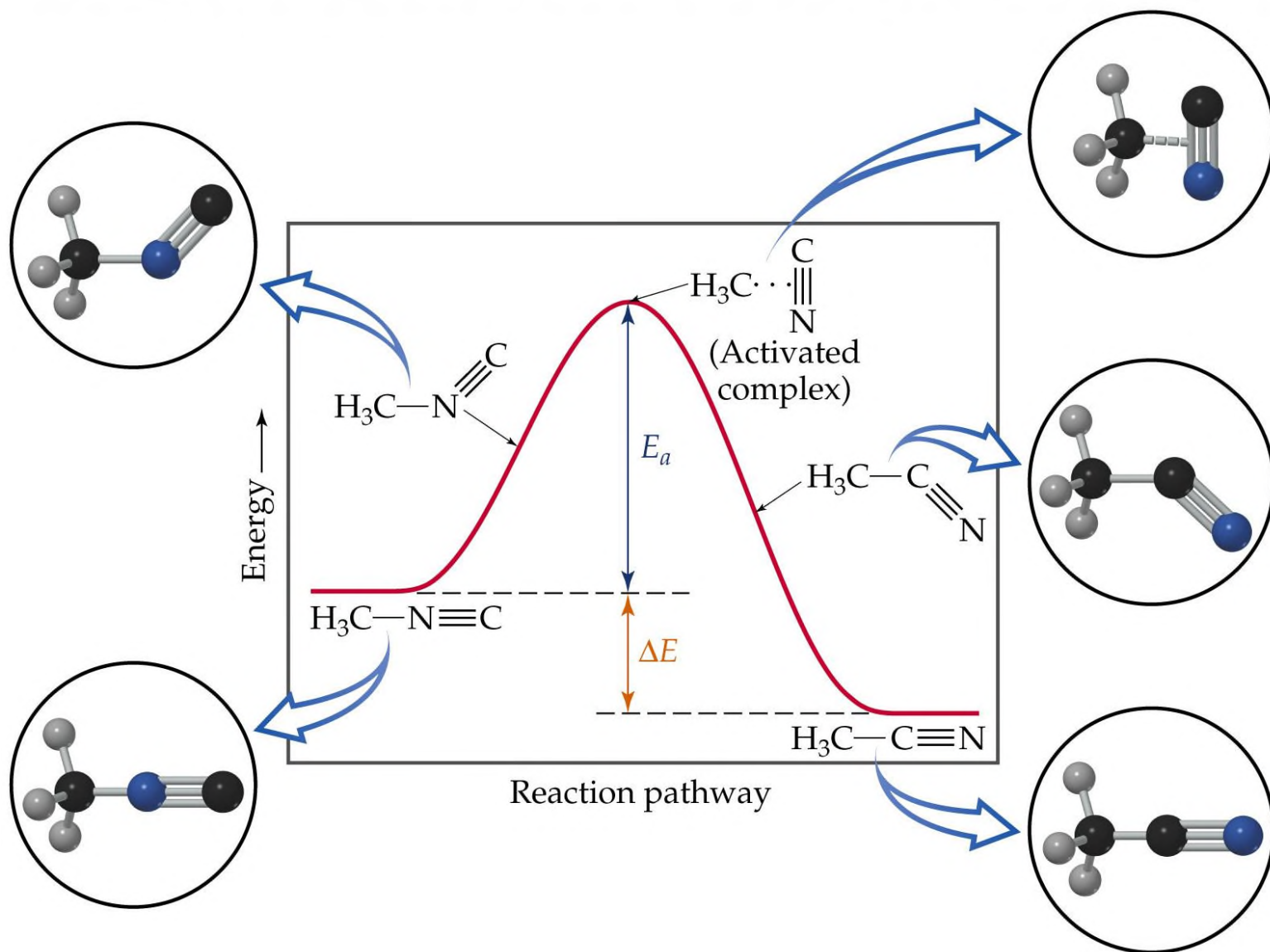
Fraction of Molecules Possessing E$_a$

- How does a methyl isonitrile molecule gain enough energy to overcome the activation energy barrier?

- From kinetic molecular theory, we know that as temperature increases, the total kinetic energy increases.

- We can show the fraction of molecules, f, with energy equal to or greater than E_a is
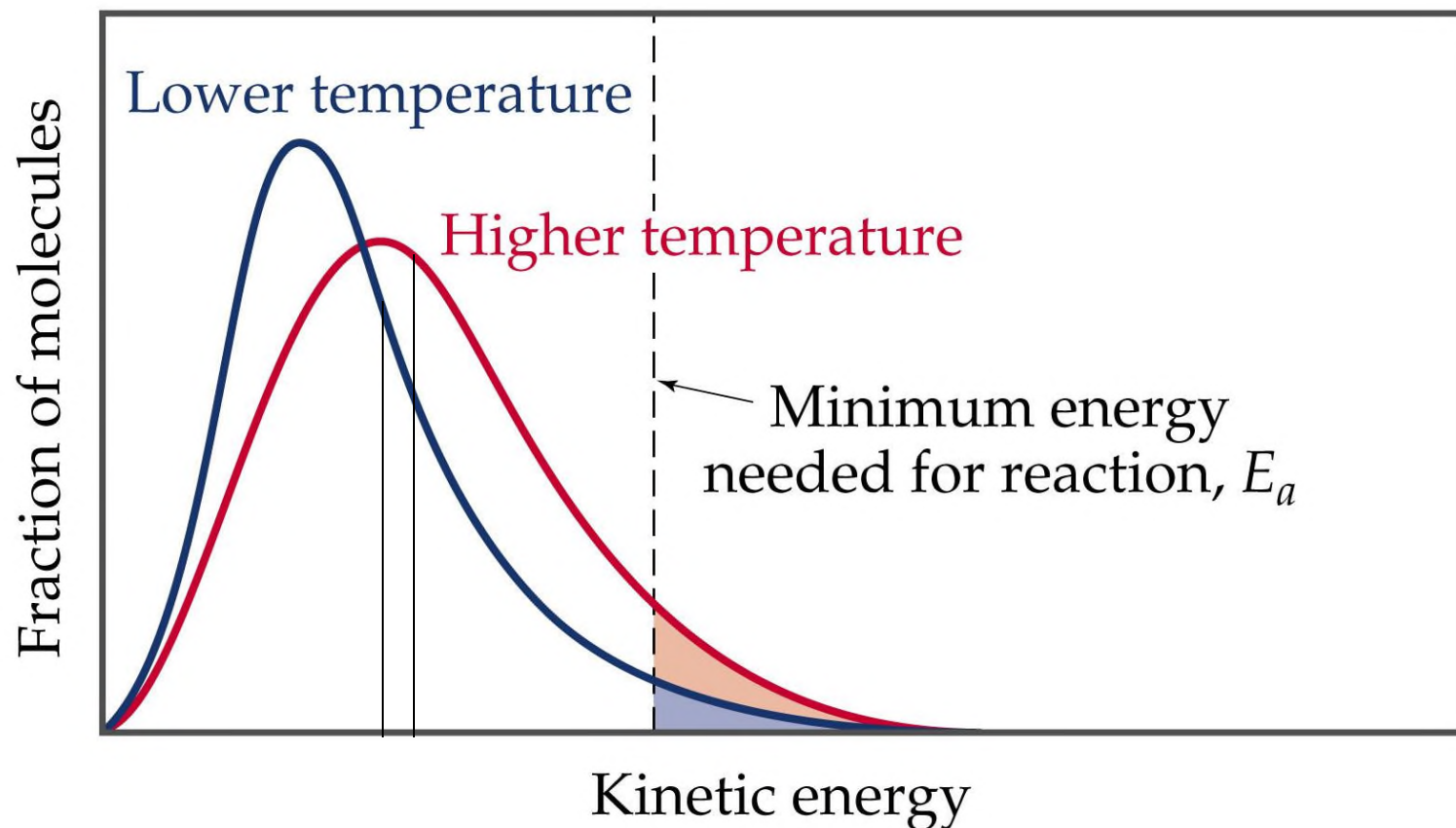
$$f = e^{-E_a/RT}$$

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

Activation Energy E_a, Plot

Boltzmann distribution of energy in gas
Room: T=298K , not all the gas molecule are the same energy
Some are lower, some are higher. T=298 just the average

The Arrhenius Equation

- Arrhenius discovered most reaction-rate data obeyed the Arrhenius equation:

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

  - k is the rate constant, E_a is the activation energy, R is the gas constant (8.314 J/K-mol) and T is the temperature in K.
  - A is called the frequency factor.
    - A is a measure of the probability of a favorable collision (or correct orientation).
  - Both A and E_a are specific to a given reaction.
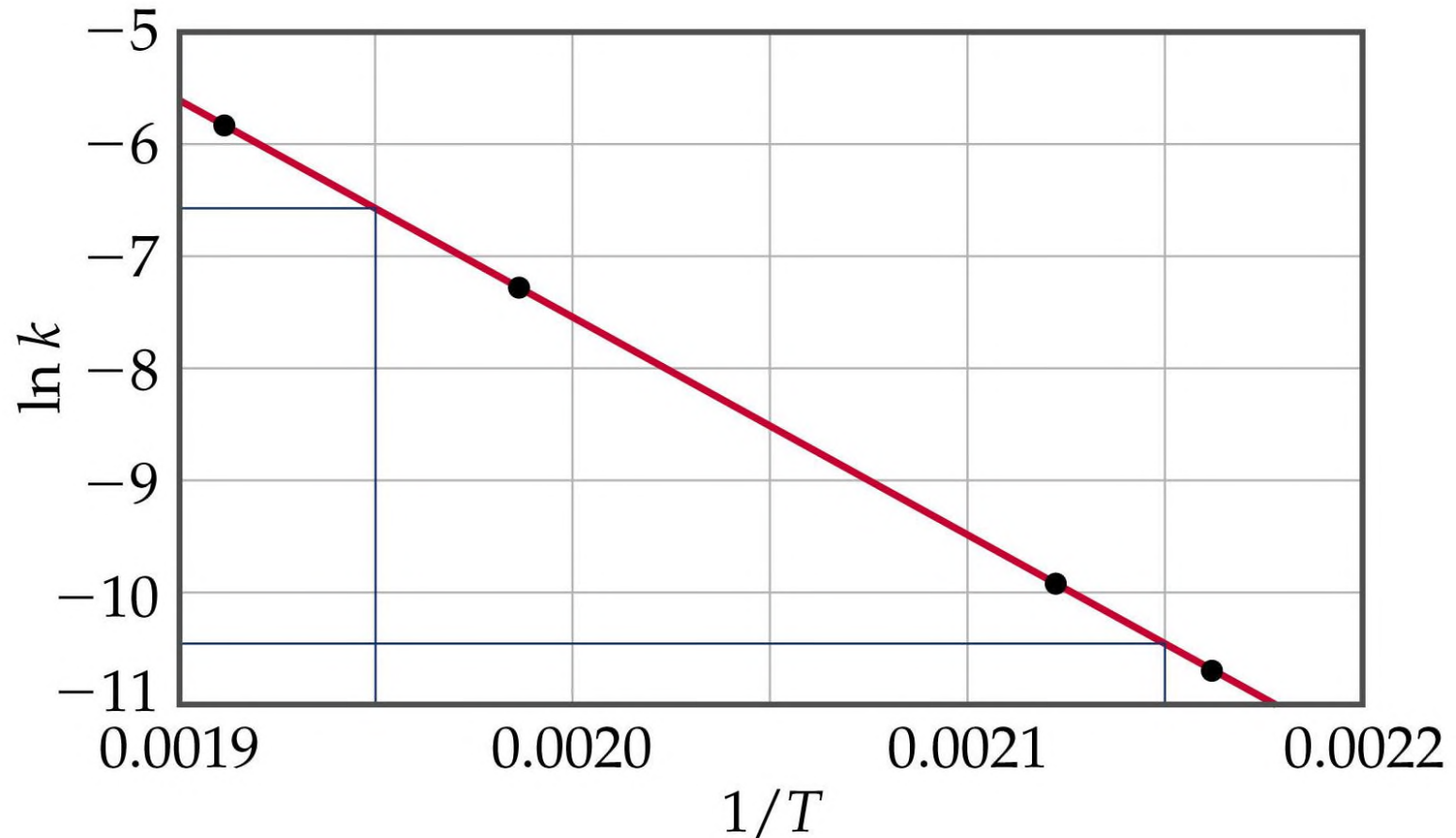
Determing Activation Energy

- If we have a lot of data, we can determine E_a and A graphically by rearranging the Arrhenius equation:

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

- From the above equation, a plot of $\ln k$ versus $1/T$ will have slope of $-E_a/R$ and intercept of $\ln A$.

Ln k versus 1/T

- E_a can be determined by finding the slope of the line.

Catalysis

- A catalyst changes the rate of a chemical reaction.
    - Increase the rate: catalyst; decrease the rate: inhibitor
    - Catalyst lower the overall E_a for a chemical reaction.
- There are two types of catalyst:
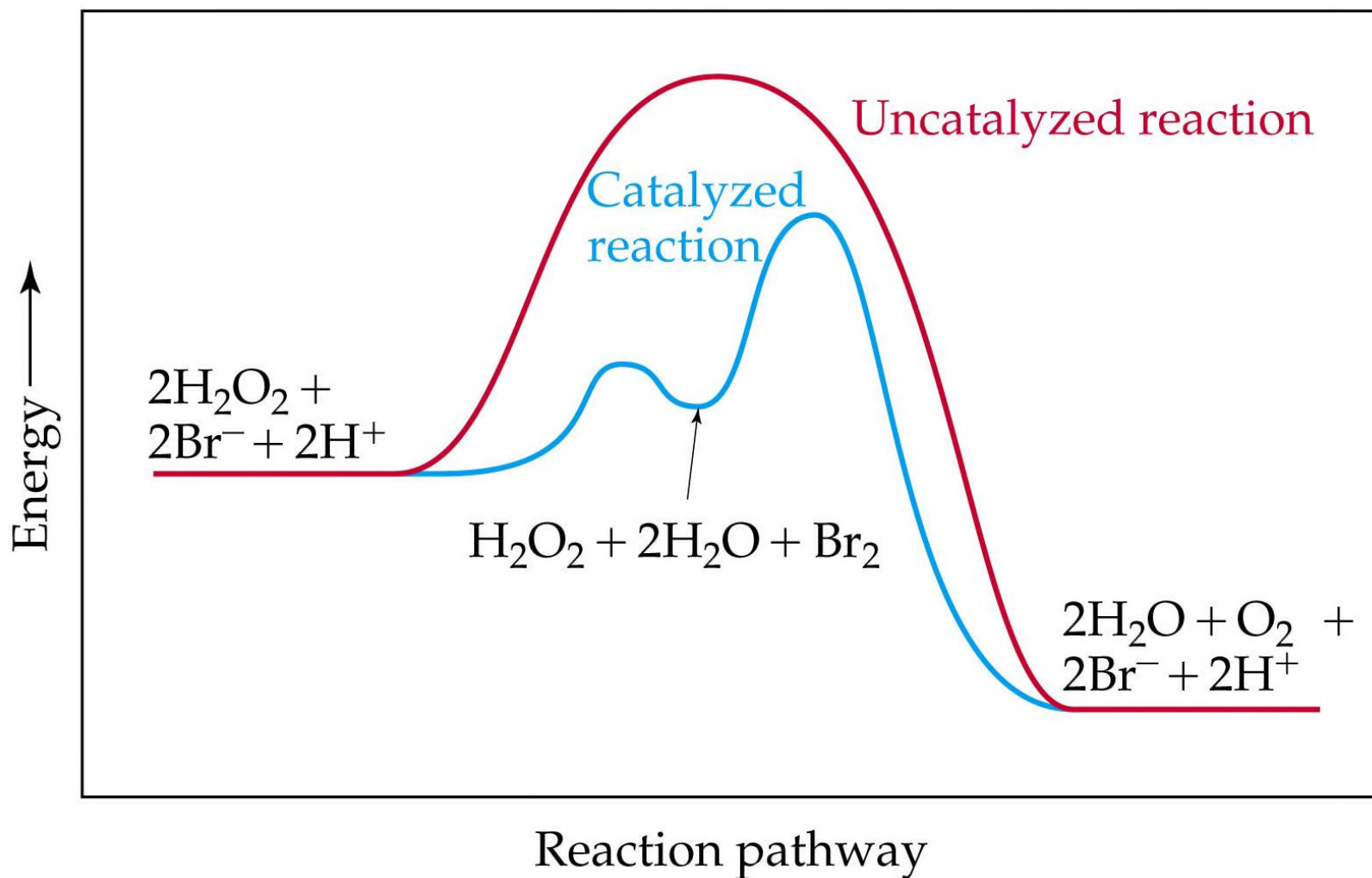   - Homogeneous and heterogeneous

Homogeneous Catalysis

- The catalyst and reaction is in one phase.
- Cl atoms are catalysts for the destruction of ozone

Heterogeneous Catalysis

- The catalyst and reaction exists in a different phase.
- Nickel is catalyst for hydrocracking of petro gas

The Effects of a Catalyst

Energy vs. Reaction pathway

$2H_2O_2 + 2Br^- + 2H^+$

Catalyzed reaction

Uncatalyzed reaction

$H_2O_2 + 2H_2O + Br_2$

$2H_2O + O_2 + 2Br^- + 2H^+$

Functions of the Catalysis

- Catalysts can operate by increasing the number of effective collisions (i.e., from the Arrhenius equation: catalysts increase k which results in increasing A or decreasing E_a.

- A catalyst may add intermediates to the reaction.

  - Example: In the presence of Br^-, $Br_2(aq)$ is generated as an intermediate in the decomposition of H_2O_2.