Chapter 15

Chemical Kinetics

Ectotherms

- Lizards and other cold-blooded creatures are **ectotherms**—animals whose body temperature matches their environment's temperature.
- When a lizard's body temperature drops, the chemical reactions that occur in its body slow down, as do all chemical reactions when cooled.
- This causes the lizard to become lethargic and to slow down.
- **Chemical kinetics** is the study of the factors that affect the rates of chemical reactions, such as temperature.

Chemical Kinetics

- The speed of a chemical reaction is called its **reaction rate**.
- The rate of a reaction is a measure of how fast the reaction makes products or uses reactants.
- The ability to control the speed of a chemical reaction is important.

$2Na + 2H_2O \longrightarrow 2NaOH + H_2$

$2H_2 + O_2 \longrightarrow 2H_2O$

Defining Rate

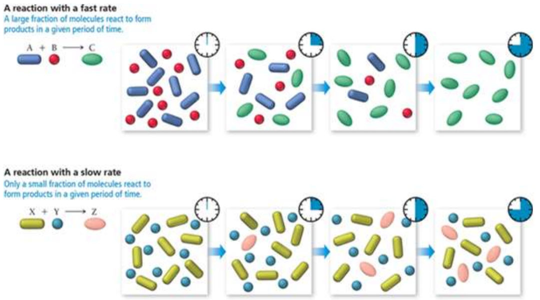
- **Rate** is how much a quantity changes in a given period of time.
- The speed you drive your car is a rate—the distance your car travels (miles) in a given period of time (1 hour).
  - So, the rate of your car has units of mi/hr.

Defining Reaction Rate

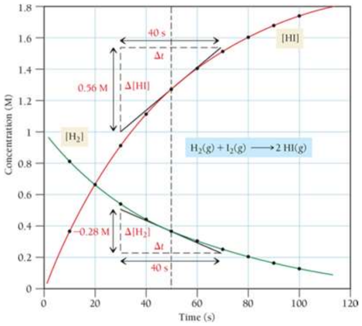
- The rate of a chemical reaction is generally measured in terms of how much the concentration of a reactant decreases (or product concentration increases) in a given period of time.
- For reactants, a negative sign is placed in front of the definition.
  - For the reaction $H_2(g) + I_2(g) \rightarrow 2\,HI(g)$

$$\text{Rate} = -\frac{\Delta[H_2]}{\Delta t} = -\frac{[H_2]_{t_2} - [H_2]_{t_1}}{t_2 - t_1}$$

Reaction Rate



Reactant and Product Concentrations as a Function of Time



$$\text{Rate} = -\frac{\Delta[H_2]}{\Delta t} = -\frac{[H_2]_{t_2} - [H_2]_{t_1}}{t_2 - t_1}$$

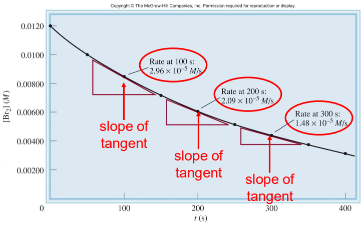
- The average rate is the change in measured concentrations in any particular time period.
  - Linear approximation of a curve
- The larger the time interval, the more the average rate deviates from the instantaneous rate.

The Average Rate of the Reaction

Time (s)	$[H_2]$ (M)	$\Delta[H_2]$ (M)	Δt (s)	Rate $= -\Delta[H_2]/\Delta t$ (M/s)
0.000	1.000	−0.181	10.000	0.0181
10.000	0.819	−0.149	10.000	0.0149
20.000	0.670	−0.121	10.000	0.0121
30.000	0.549	−0.100	10.000	0.0100
40.000	0.449	−0.081	10.000	0.0081
50.000	0.368	−0.067	10.000	0.0067
60.000	0.301	−0.054	10.000	0.0054
70.000	0.247	−0.045	10.000	0.0045
80.000	0.202	−0.037	10.000	0.0037
90.000	0.165	−0.030	10.000	0.0030
100.000	0.135			

Instantaneous Rate

- The instantaneous rate is the change in concentration at any one particular time.
  - Slope at one point of a curve
- The instantaneous rate is determined by taking the slope of a line tangent to the curve at that particular point.
  - First derivative of the function (for all of you calculus fans)


Copyright © The McGraw-Hill Companies, Inc. Permission required for reproduction or display.

Rate changes with [conc]

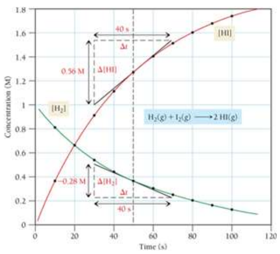
rate α [Br$_2$]

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

instantaneous rate = rate for specific instance in time

We need a better way to describe the rate!

$H_2(g) + I_2(g) \rightarrow 2\,HI(g)$



Using $[H_2]$, the instantaneous rate at 50 s is as follows:

$$\text{Rate} = -\frac{-0.28\ \text{M}}{40\ \text{s}}$$

$$\text{Rate} = 0.0070\frac{\text{M}}{\text{s}}$$

Using [HI], the instantaneous rate at 50 s is as follows:

$$\text{Rate} = \left(\frac{1}{2}\right)\frac{0.56\ \text{M}}{40\ \text{s}}$$

$$\text{Rate} = 0.0070\frac{\text{M}}{\text{s}}$$

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.

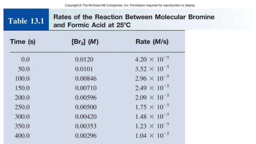


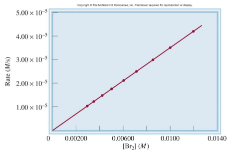
Table 13.1 Rates of the Reaction Between Molecular Bromine and Formic Acid at 25°C

Time (s)	$[Br_2]$ (*M*)	Rate (*M*/s)
0.0	0.0120	4.20×10^{-5}
50.0	0.0101	3.52×10^{-5}
100.0	0.00846	2.96×10^{-5}
150.0	0.00710	2.49×10^{-5}
200.0	0.00596	2.09×10^{-5}
250.0	0.00500	1.75×10^{-5}
300.0	0.00420	1.48×10^{-5}
350.0	0.00353	1.23×10^{-5}
400.0	0.00296	1.04×10^{-5}

$$\text{rate} = k\,[Br_2] + 0$$

$$k = \frac{\text{rate}}{[Br_2]} = \textbf{\textit{rate constant}}$$

$$= 3.50 \times 10^{-3}\ s^{-1}$$



rate constant- constant of the proportionality between the reaction rate and the concentration of reactant.

General descriptor for the rate of a reaction that is independent of [conc].

Reaction Rate and Stoichiometry

- In most reactions, the coefficients of the balanced equation are not all the same.

$$H_2(g) + I_2(g) \rightarrow 2\,HI(g)$$

- For these reactions, the change in the number of molecules of one substance is a multiple of the change in the number of molecules of another.
  - For the above reaction, for every 1 mole of H_2 used, 1 mole of I_2 will also be used and 2 moles of HI made.
  - Therefore, the rate of change will be different.
- To be consistent, the change in the concentration of each substance is multiplied by 1/coefficient.

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

Question

For the reaction A + 2B → C under a given set of conditions, the initial rate is 0.100 M/s. What is $\frac{\Delta[\mathrm{B}]}{\Delta t}$ under the same conditions?

a. −0.0500 M/s
b. −0.100 M/s
c. −0.200 M/s
d. +0.200 M/s

Answer

For the reaction A + 2B → C under a given set of conditions, the initial rate is 0.100 M/s. What is $\frac{\Delta[\mathrm{B}]}{\Delta t}$ under the same conditions?

a. −0.0500 M/s
b. −0.100 M/s
c. −0.200 M/s
d. +0.200 M/s

Measuring Reaction Rate

- To measure the reaction rate you need to be able to measure the concentration of at least one component in the mixture at many points in time.
- Some reactions occur slowly enough that samples can be periodically withdrawn from the reaction vessel and analyzed to determine the progress of the reaction.
- Three techniques are commonly used to monitor a reaction mixture: polarimetry, spectroscopy, and pressure measurement.

Continuous Monitoring

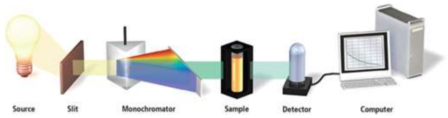
- **Polarimetry**—This measures the change in the degree of rotation of plane-polarized light caused by one of the components over time.
- **Spectrophotometry**—This measures the amount of light of a particular wavelength absorbed by one component over time.
  - The component absorbs its complementary color.
- **Total pressure**—The total pressure of a gas mixture is stoichiometrically related to partial pressures of the gases in the reaction.

Sampling the Reaction Mixture at Specific Times

- **Aliquots** (samples from the reaction mixture) are drawn off at specific times during the reaction, and quantitative analysis is performed.
  - Titration for one of the components
  - Gravimetric analysis
- **Gas chromatography** can measure the concentrations of various components in a mixture.
  - For samples that have volatile components
  - Separates mixture by adherence to a surface

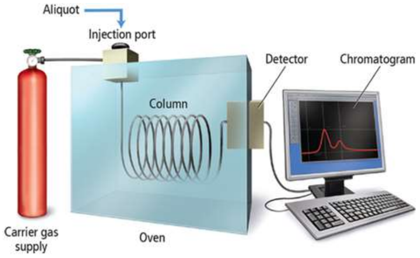
Methods for Determining Concentrations in a Mixture

(1 of 2)



Methods for Determining Concentrations in a Mixture

(2 of 2)



Factors Affecting Reaction Rate: Reactant Concentration

- Rate often depends on the concentration of one or more of the reactant molecules.
- **Rate law** is an equation relating concentration of reactants to rate when the reverse reaction is negligible.

The Rate Law

- The rate of a reaction is directly proportional to the concentration of each reactant raised to a power.
- For the reaction **A** → **products**, the rate law would have the form given below.

$$\text{Rate} = k\left[\text{A}\right]^n$$

  - n is called the **order**; usually, it is an integer that determines rate dependence on reactant concentration.
  - k is called the **rate constant**.

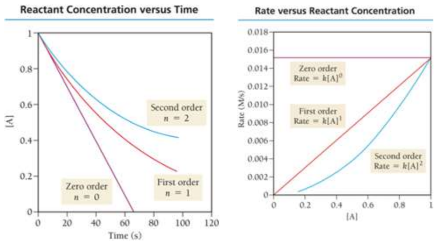
Reaction Order

- The exponent on each reactant in the rate law is called the **order** with respect to that reactant.
- The sum of the exponents on the reactants is called the **order of the reaction**.
- In the rate law, Rate = *k*[NO]2[O_2], the reaction is second order with respect to [NO], first order with respect to [O_2], and third order overall.

Rate = *k*[A]^n

- If a reaction is zero order, the rate of the reaction is always the same.
  - Doubling [A] will have no effect on the reaction rate.
- If a reaction is first order, the rate is directly proportional to the reactant concentration.
  - Doubling [A] will double the rate of the reaction.
- If a reaction is second order, the rate is directly proportional to the square of the reactant concentration.
  - Doubling [A] will quadruple the rate of the reaction.

Reactant Concentration Versus Time
A → Products



Question

For a particular reaction in which A → products, a doubling of the concentration of A causes the reaction rate to double. What is the order of the reaction?

a. 0

b. 1

c. 2

Answer

For a particular reaction in which A → products, a doubling of the concentration of A causes the reaction rate to double. What is the order of the reaction?

a. 0

b. 1

c. 2

Determining the Order of a Reaction

- The rate law **must** be determined experimentally.
- We can use the **method of initial rates**, where data from different experiments with varying starting concentrations of reactants and the corresponding initial rates are given.
- Determine how rate is impacted by change in a single reactant in two different experiments.

Integrated Rate Laws

- The rate law shows the relationship between rate and concentration.
  - Relates rate and concentration via rate constant.
  - Tells you the order of the reaction.
  - Rate constant is good for comparing different reactions.
- It is useful to have an equation relating concentration with time.
- Using calculus, we can obtain the **integrated rate law** that shows the relationship between the concentration of A and the time of the reaction.

Summary of the Kinetics of Zero-Order, First-Order and Second-Order Reactions

Order	Rate Law	Concentration-Time Equation	Half-Life
0	rate = k	$[A] = [A]_0 - kt$	$t_{½} = \frac{[A]_0}{2k}$
1	rate = k [A]	$\ln[A] = \ln[A]_0 - kt$	$t_{½} = \frac{\ln 2}{k}$
2	rate = k $[A]^2$	$\frac{1}{[A]} = \frac{1}{[A]_0} + kt$	$t_{½} = \frac{1}{k[A]_0}$

Can also be used, with minor modification, to predict concentrations at any time and vice versa!

General rate law

$$rate = k[\mathrm{A}]^x[\mathrm{B}]^y$$

First Order Reactions

Rate law can also be used, with minor modification, to predict concentrations at any time and vice versa!

$$\mathrm{A} \longrightarrow \mathrm{B}$$

Reaction rate:

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

Rate Law:

$$\text{rate} = k\,[A]$$

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

Calculus Happens!

In differential form, Equation (13.2) becomes

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

Rearranging, we get

$$-\frac{d[A]}{[A]} = -kdt$$

Integrating between $t = 0$ and $t = t$ gives

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

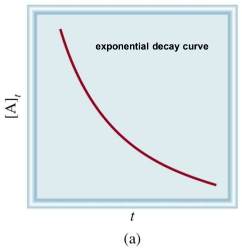
$$\ln[A]_t - \ln[A]_0 = -kt$$

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

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

First Order Reactions

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



(a)

t is time

$[A]_t$ is the concentration of A at any time t

$[A]_0$ is the concentration of A at time t=0

k is the rate constant

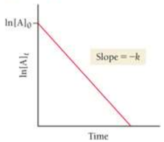
$$y = m \cdot x + b$$

$$\ln[A]_t = -k \cdot t + \ln[A]_0$$

- Know $[A]_0$ and t, predict $[A]_t$
- Know $[A]_0$ and $[A]_t$, predict t
- Know $[A]_t$ and t, predict $[A]_0$

First-Order Integrated Rate Law

A plot of the natural log of the reactant concentration as a function of time yields a straight line.



Question

The reaction A → B has been experimentally determined to be second order. The initial rate is 0.0100 M/s at an initial concentration of A of 0.100 M. What is the initial rate at [A] = 0.500 M ?

a. 0.00200 M/s

b. 0.0100 M/s

c. 0.0500 M/s

d. 0.250 M/s

Answer

The reaction A → B has been experimentally determined to be second order. The initial rate is 0.0100 M/s at an initial concentration of A of 0.100 M. What is the initial rate at [A] = 0.500 M ?

a. 0.00200 M/s

b. 0.0100 M/s

c. 0.0500 M/s

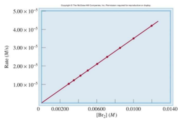
d. 0.250 M/s

Determination of *k*

Earlier we found k by graphing Rate vs [conc]

$$\text{rate} = k\,[Br_2]$$

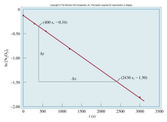
But you have to calc rate at each [conc] and then find the slope.



$$2N_2O_5 \longrightarrow 4NO_2\,(g) + O_2\,(g)$$

t (s)	[N₂O₅] (*M*)	ln [N₂O₅]
0	0.91	−0.094
300	0.75	−0.29
600	0.64	−0.45
1200	0.44	−0.82
3000	0.16	−1.83

Measure concentration with time.



Graph date.

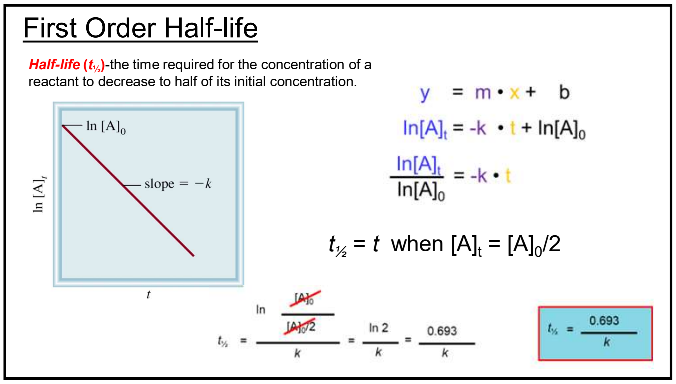
$$y = m \bullet x + b$$

$$\ln[A]_t = -k \bullet t + \ln[A]_0$$

$$m = -k$$

$$k = 5.7 \times 10^{-4}\ s^{-1}$$

Math.



First Order Half-life

***Half-life* ($t_{1/2}$)**-the time required for the concentration of a reactant to decrease to half of its initial concentration.

$$y \;=\; m \cdot x + b$$

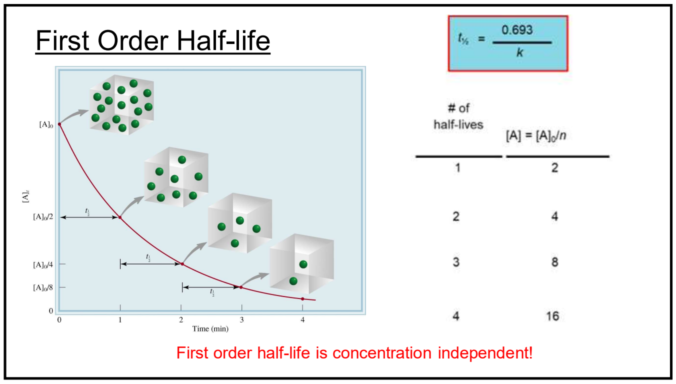
$$\ln[A]_t = -k \cdot t + \ln[A]_0$$

$$\frac{\ln[A]_t}{\ln[A]_0} = -k \cdot t$$

$t_{1/2} = t$ when $[A]_t = [A]_0/2$

$$t_{1/2} = \frac{\ln \dfrac{\cancel{[A]_0}}{\cancel{[A]_0}/2}}{k} = \frac{\ln 2}{k} = \frac{0.693}{k}$$

$$\boxed{t_{1/2} = \frac{0.693}{k}}$$



First Order Half-life

$$\boxed{t_{1/2} = \frac{0.693}{k}}$$

# of half-lives	[A] = [A]$_0$/*n*
1	2
2	4
3	8
4	16

First order half-life is concentration independent!

Radioactive decay as 1st order rxns

Many radioactive decay processes are first order…

$${}^{131}_{53}\mathrm{I} \xrightarrow{\beta^- \text{ decay}} {}^{131}_{54}\mathrm{Xe} + \bar{\nu} + e^-$$ half-life of 8.04 days

$${}^{14}_{6}\mathrm{C} \xrightarrow{\beta^- \text{ decay}} {}^{14}_{7}\mathrm{N} + \bar{\nu} + e^-$$ half-life of 5730 yrs

$${}^{238}_{92}\mathrm{U} \xrightarrow{\alpha \text{ decay}} {}^{234}_{90}\mathrm{Th} + {}^{4}_{2}\mathrm{He}^{2+}$$ half-life of 4.51 x 10^9 yrs

Radiometric Dating-

An error margin of 2–5% has been achieved on dating younger Mesozoic rocks (252-266 million years old). Typically, with uranium doped $ZrSiO_4$.

${}^{238}U$ to ${}^{206}Pb$

${}^{14}C$ radiometric dating.

Ratio of ${}^{14}C$ to ${}^{12}C$

Determining the Rate Law When There Are Multiple Reactants (1 of 2)

- Changing each reactant will affect the overall rate of the reaction.
- By changing the initial concentration of one reactant at a time, the effect of each reactant's concentration on the rate can be determined.
- In examining results, we compare differences in rate for reactions that differ only in the concentration of one reactant.

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

- where m is the reaction order with respect to A and n

Determining the Rate Law When There Are Multiple Reactants (2 of 2)

- We determine the order of each reactant from experimental data.
- The resulting rate law would have the following form.

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

where m is the reaction order with respect to A and n is the reaction order with respect to B

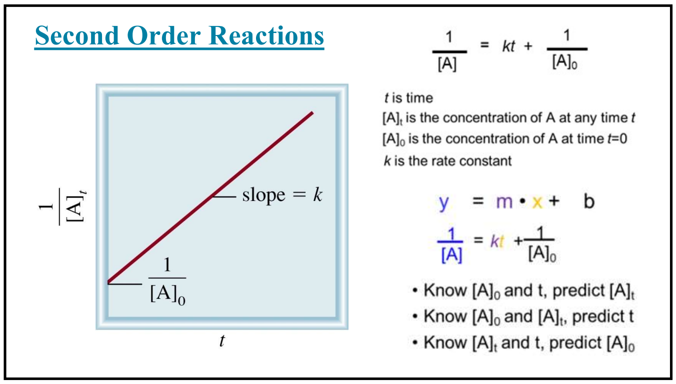
- The reaction is said to have an **overall order** of (m+n)

The decomposition of ethane (C_2H_6) to methyl radicals is a first-order reaction with a rate constant of $5.36 \times 10^{-4}\ s^{-1}$ at 700°C:

$$C_2H_6(g) \longrightarrow 2CH_3(g)$$

Calculate the half-life of the reaction in minutes.

$$\begin{aligned} t_{\frac{1}{2}} &= \frac{0.693}{k} \\ &= \frac{0.693}{5.36 \times 10^{-4}\ \text{s}^{-1}} \\ &= 1.29 \times 10^{3}\ \text{s} \times \frac{1\ \text{min}}{60\ \text{s}} \\ &= 21.5\ \text{min} \end{aligned}$$



Second Order Reactions

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

t is time

$[A]_t$ is the concentration of A at any time t

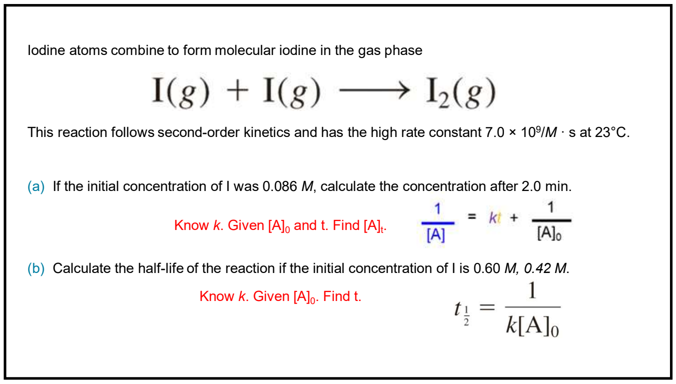
$[A]_0$ is the concentration of A at time t=0

k is the rate constant

$$y = m \cdot x + b$$

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

- Know $[A]_0$ and t, predict $[A]_t$
- Know $[A]_0$ and $[A]_t$, predict t
- Know $[A]_t$ and t, predict $[A]_0$



Iodine atoms combine to form molecular iodine in the gas phase

$$I(g) + I(g) \longrightarrow I_2(g)$$

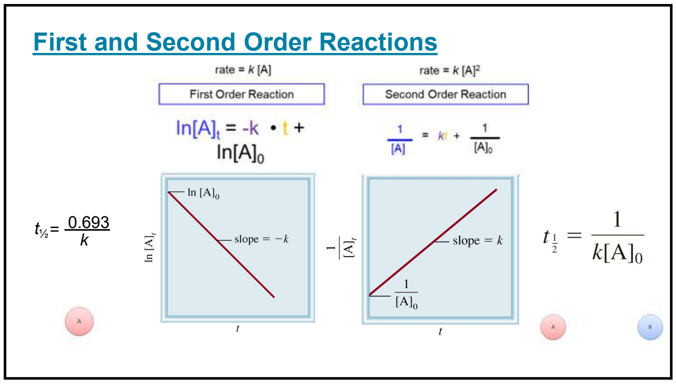
This reaction follows second-order kinetics and has the high rate constant 7.0 × $10^9/M \cdot s$ at 23°C.

(a) If the initial concentration of I was 0.086 *M*, calculate the concentration after 2.0 min.

Know *k*. Given $[A]_0$ and t. Find $[A]_t$. $\frac{1}{[A]} = kt + \frac{1}{[A]_0}$

(b) Calculate the half-life of the reaction if the initial concentration of I is 0.60 *M*, *0.42 M*.

Know *k*. Given $[A]_0$. Find t. $t_{\frac{1}{2}} = \frac{1}{k[A]_0}$

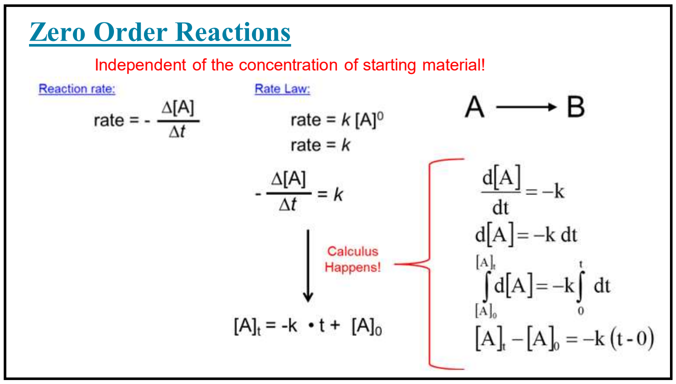


First and Second Order Reactions

rate = k [A]	rate = k $[A]^2$
First Order Reaction	Second Order Reaction
$\ln[A]_t = -k \cdot t + \ln[A]_0$	$\frac{1}{[A]} = kt + \frac{1}{[A]_0}$

$$t_{½} = \frac{0.693}{k}$$

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



Zero Order Reactions

Independent of the concentration of starting material!

Reaction rate:

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

Rate Law:

$$\text{rate} = k[A]^0$$

$$\text{rate} = k$$

$$A \longrightarrow B$$

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

Calculus Happens!

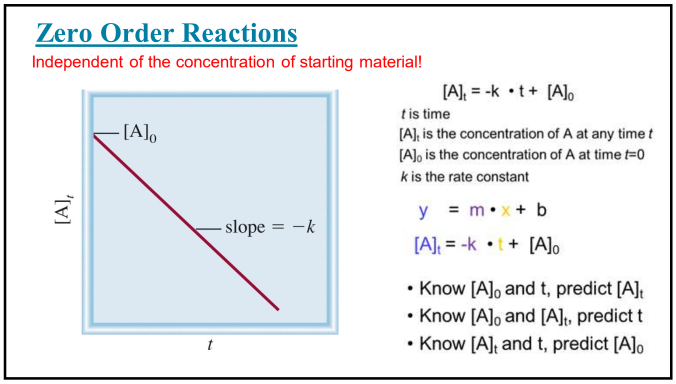
$$\frac{d[A]}{dt} = -k$$

$$d[A] = -k\,dt$$

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

$$[A]_t - [A]_0 = -k(t-0)$$

$$[A]_t = -k \cdot t + [A]_0$$



Zero Order Reactions

Independent of the concentration of starting material!

$$[A]_t = -k \cdot t + [A]_0$$

t is time

$[A]_t$ is the concentration of A at any time *t*

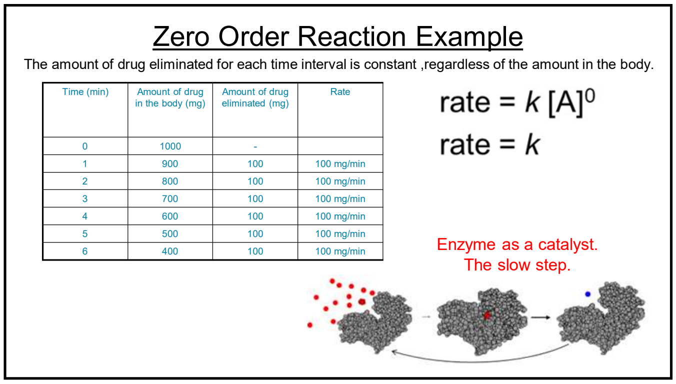
$[A]_0$ is the concentration of A at time *t*=0

k is the rate constant

$$y = m \cdot x + b$$

$$[A]_t = -k \cdot t + [A]_0$$

- Know $[A]_0$ and t, predict $[A]_t$
- Know $[A]_0$ and $[A]_t$, predict t
- Know $[A]_t$ and t, predict $[A]_0$



Zero Order Reaction Example

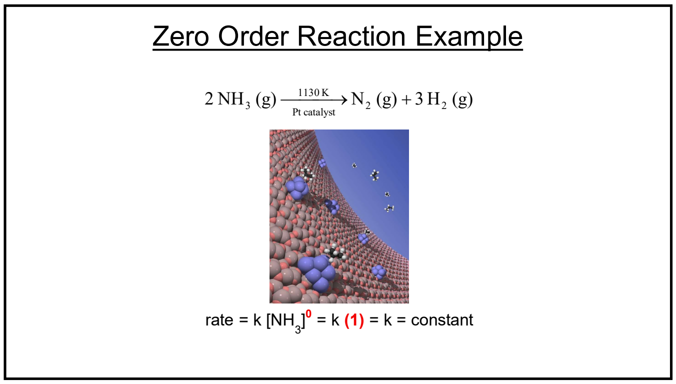
The amount of drug eliminated for each time interval is constant ,regardless of the amount in the body.

Time (min)	Amount of drug in the body (mg)	Amount of drug eliminated (mg)	Rate
0	1000	-	
1	900	100	100 mg/min
2	800	100	100 mg/min
3	700	100	100 mg/min
4	600	100	100 mg/min
5	500	100	100 mg/min
6	400	100	100 mg/min

$$\text{rate} = k[A]^0$$

$$\text{rate} = k$$

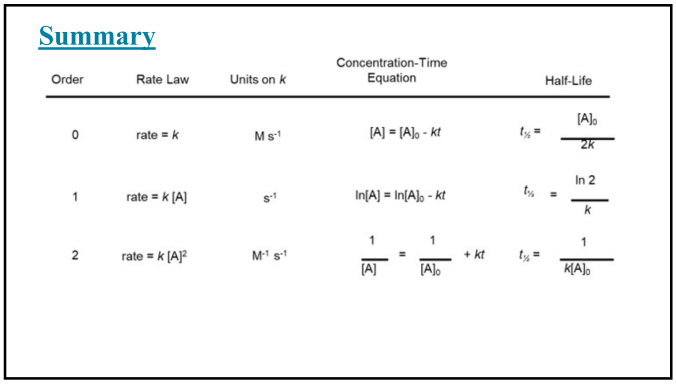
Enzyme as a catalyst.
The slow step.



Zero Order Reaction Example

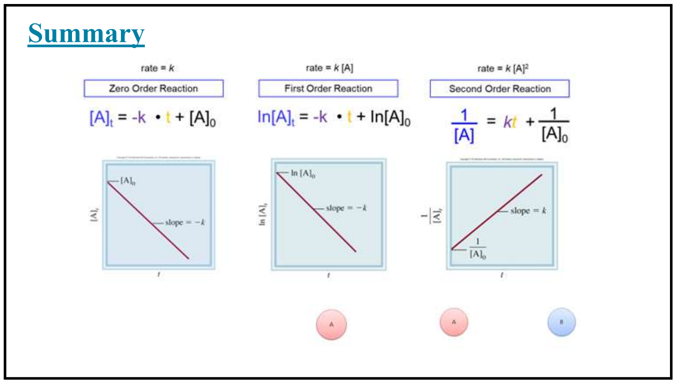
$$2\,NH_3\,(g) \xrightarrow[\text{Pt catalyst}]{1130\,K} N_2\,(g) + 3\,H_2\,(g)$$

rate = k $[NH_3]^0$ = k (1) = k = constant



Summary

Order	Rate Law	Units on k	Concentration-Time Equation	Half-Life
0	rate = k	M s^{-1}	$[A] = [A]_0 - kt$	$t_{½} = \frac{[A]_0}{2k}$
1	rate = k [A]	s^{-1}	$\ln[A] = \ln[A]_0 - kt$	$t_{½} = \frac{\ln 2}{k}$
2	rate = $k\,[A]^2$	$M^{-1}\ s^{-1}$	$\frac{1}{[A]} = \frac{1}{[A]_0} + kt$	$t_{½} = \frac{1}{k[A]_0}$



Summary

rate = k

Zero Order Reaction

$[A]_t = -k \bullet t + [A]_0$

rate = k [A]

First Order Reaction

$\ln[A]_t = -k \bullet t + \ln[A]_0$

rate = $k\,[A]^2$

Second Order Reaction

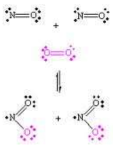
$\frac{1}{[A]} = kt + \frac{1}{[A]_0}$

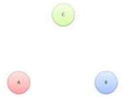
Side note: Third Order Kinetics

Rare and typically slow!

$2NO + O_2 \rightarrow 2NO_2$

$$\frac{d[NO_2]}{dt} = k\,[NO]^2[O_2]$$



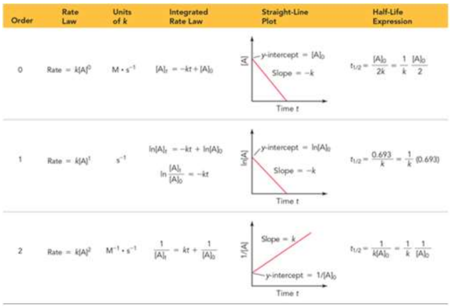


One possibility for the mechanism of this reaction would be a three-body collision (i.e. a true termolecular reaction).

Note: Units of k tells you the RO

$$\mathrm{rate} = k[\mathrm{A}]^m[\mathrm{B}]^n$$

$$\mathrm{M/s} = k\ \ \mathrm{M}^m\ \ \mathrm{M}^n$$



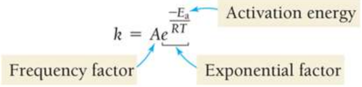
Order	Rate Law	Units of *k*	Integrated Rate Law	Straight-Line Plot	Half-Life Expression
0	Rate = $k[A]^0$	$M \cdot s^{-1}$	$[A]_t = -kt + [A]_0$	[A] y-intercept = $[A]_0$ Slope = $-k$ Time *t*	$t_{1/2} = \frac{[A]_0}{2k} = \frac{1}{k}\frac{[A]_0}{2}$
1	Rate = $k[A]^1$	s^{-1}	$\ln[A]_t = -kt + \ln[A]_0$ $\ln\frac{[A]_t}{[A]_0} = -kt$	ln[A] y-intercept = $\ln[A]_0$ Slope = $-k$ Time *t*	$t_{1/2} = \frac{0.693}{k} = \frac{1}{k}(0.693)$
2	Rate = $k[A]^2$	$M^{-1} \cdot s^{-1}$	$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$	1/[A] Slope = k y-intercept = $1/[A]_0$ Time *t*	$t_{1/2} = \frac{1}{k[A]_0} = \frac{1}{k}\frac{1}{[A]_0}$

Summarizing Basic Kinetics Relationships

- The reaction order and rate law must be determined experimentally.
- The rate law relates the rate of the reaction to the concentration of the reactant(s).
- The integrated rate law (which is mathematically derived from the rate law) relates the concentration of the reactant(s) to time.
- The half-life is the time it takes for the concentration of a reactant to fall to one-half of its initial value.
- The half-life of a first-order reaction is independent of the initial concentration.
- The half-lives of zero-order and second-order reactions depend on the initial concentrations.

The Effect of Temperature on Rate

- The rate constant of the rate law, *k*, is temperature dependent.
- The **Arrhenius equation** shows the relationship:



$$k = Ae^{\frac{-E_a}{RT}}$$

where *T* is the temperature in kelvin

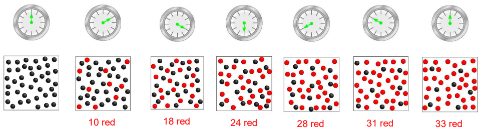
R is the gas constant in energy units, 8.314 J / (mol·K)

A is called the **frequency factor**, the rate the reactant energy approaches the activation energy

E_a is the **activation energy**, the minimum energy needed to start the reaction

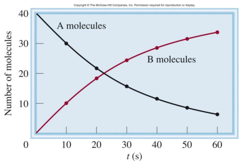
---

A ⟶ B



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

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


Copyright © The McGraw-Hill Companies, Inc. Permission required for reproduction or display.

Chemical Reactions

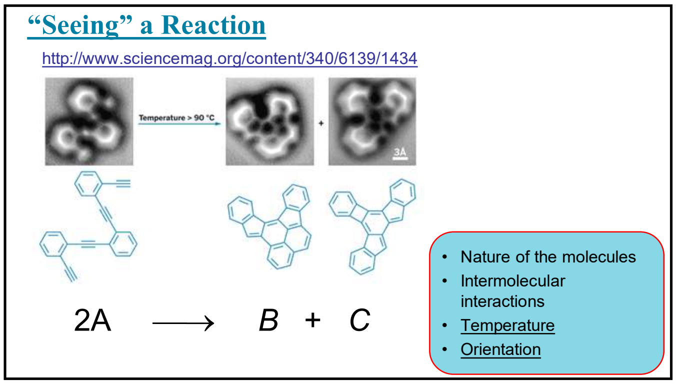
- Process Dynamics
- Abstract concept (A to B, orange to clear)
- Molecules
  - Have a size and shape.
  - Have distributions of kinetic energies.

$$A \longrightarrow B$$

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

$$\text{rate} = k\,[A]$$

$$\ln[A]_t = -k \cdot t + \ln[A]_0$$



“Seeing” a Reaction

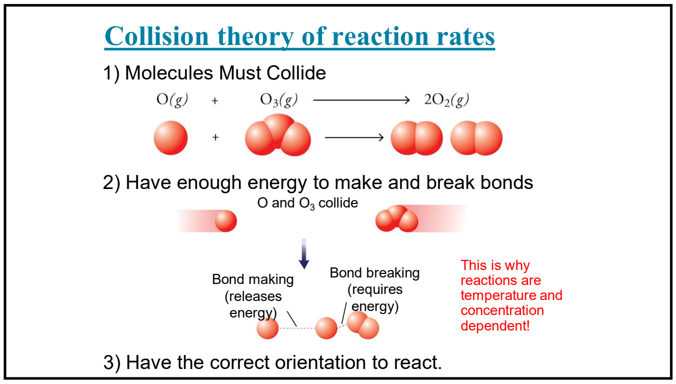
http://www.sciencemag.org/content/340/6139/1434

Temperature > 90 °C

3Å

2A ⟶ *B* + *C*

- Nature of the molecules
- Intermolecular interactions
- Temperature
- Orientation



Collision theory of reaction rates

1) Molecules Must Collide

$O(g) + O_3(g) \longrightarrow 2O_2(g)$

2) Have enough energy to make and break bonds

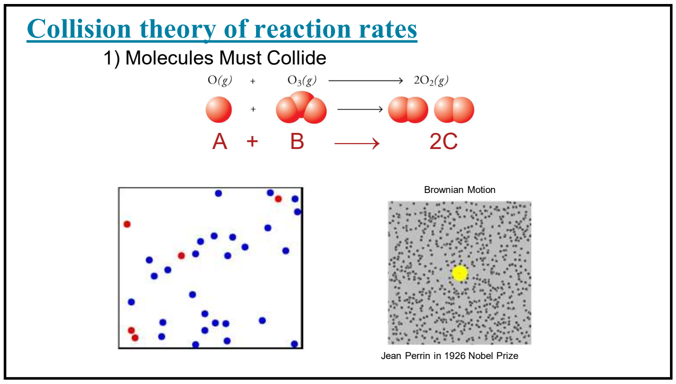
O and O_3 collide

Bond making (releases energy)

Bond breaking (requires energy)

This is why reactions are temperature and concentration dependent!

3) Have the correct orientation to react.



Collision theory of reaction rates

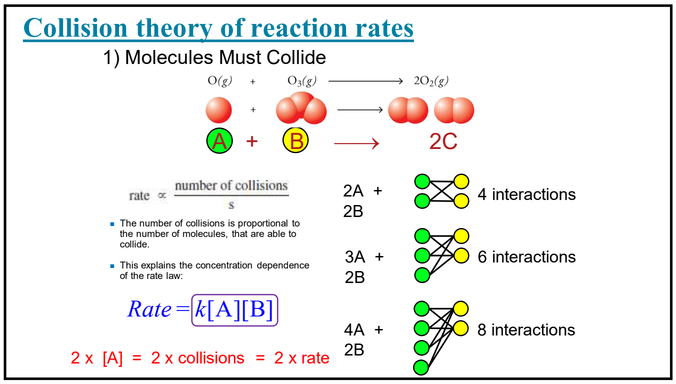
1) Molecules Must Collide

$O(g) + O_3(g) \longrightarrow 2O_2(g)$

A + B ⟶ 2C

Brownian Motion

Jean Perrin in 1926 Nobel Prize



Collision theory of reaction rates

1) Molecules Must Collide

$O(g) + O_3(g) \longrightarrow 2O_2(g)$

A + B ⟶ 2C

$$\text{rate} \propto \frac{\text{number of collisions}}{\text{s}}$$

- The number of collisions is proportional to the number of molecules, that are able to collide.
- This explains the concentration dependence of the rate law:

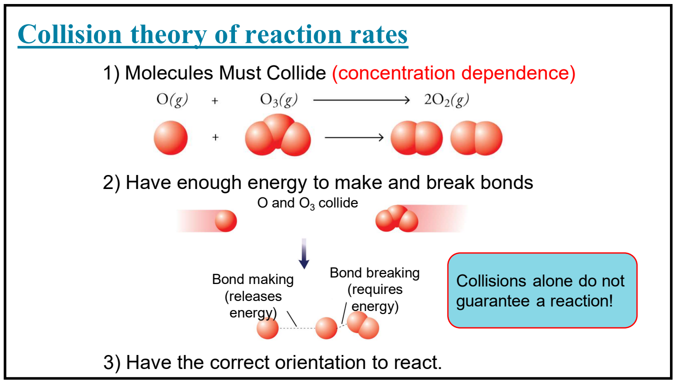
$$Rate = \boxed{k[A][B]}$$

2 x [A] = 2 x collisions = 2 x rate

2A + 2B 4 interactions

3A + 2B 6 interactions

4A + 2B 8 interactions



Collision theory of reaction rates

1) Molecules Must Collide (concentration dependence)

$O(g) + O_3(g) \longrightarrow 2O_2(g)$

2) Have enough energy to make and break bonds

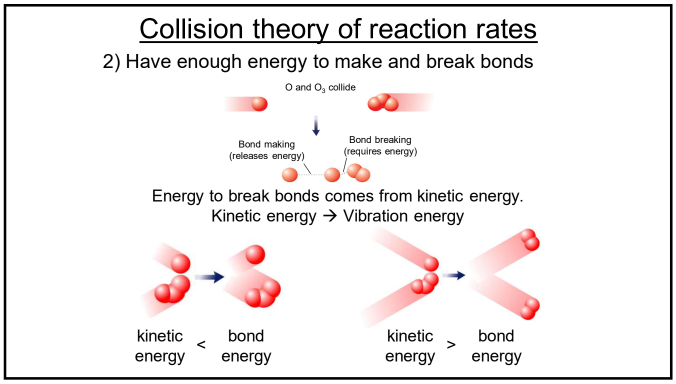
O and O_3 collide

Bond making (releases energy)

Bond breaking (requires energy)

Collisions alone do not guarantee a reaction!

3) Have the correct orientation to react.



Collision theory of reaction rates

2) Have enough energy to make and break bonds

O and O_3 collide

Bond making (releases energy)

Bond breaking (requires energy)

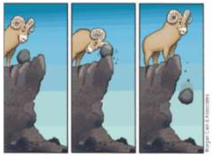
Energy to break bonds comes from kinetic energy.
Kinetic energy → Vibration energy

kinetic energy < bond energy

kinetic energy > bond energy

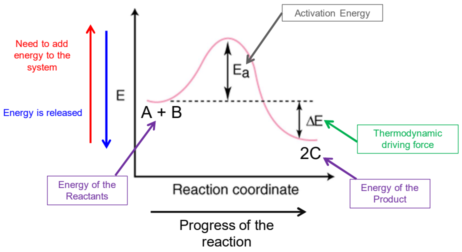
Collision theory of reaction rates

- ***Activation energy*** (E_a)- the minimum energy that must be overcome for the reaction to occur.
  - 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.



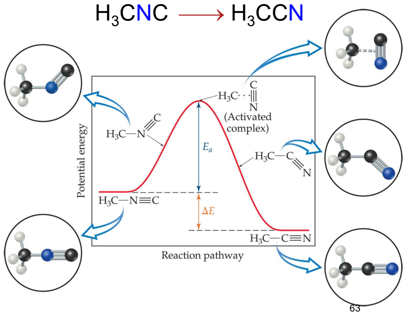
Reaction Coordinate Diagram

$A + B \longrightarrow 2C$



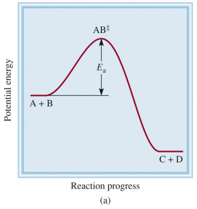
Reaction Coordinate Diagram

$H_3CNC \longrightarrow H_3CCN$

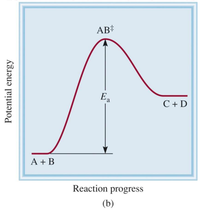


Reaction Coordinate Diagram

Exothermic Reaction



Endothermic Reaction

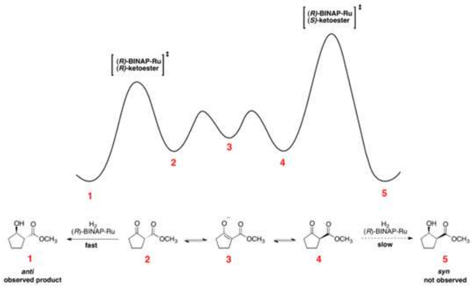


Energy$_{\text{products}}$ < Energy$_{\text{reactants}}$

Energy$_{\text{products}}$ > Energy$_{\text{reactants}}$

Reaction Coordinate Diagram

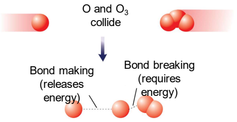
They get fun/complex!

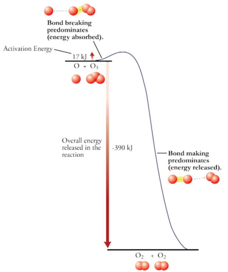


Collision theory of reaction rates

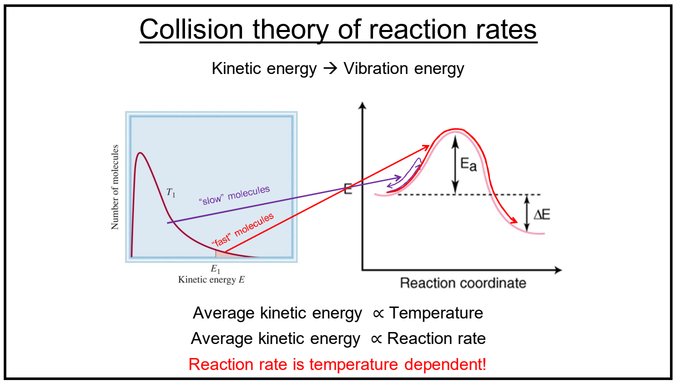
2) Have enough energy to make and break bonds

$$O(g) + O_3(g) \longrightarrow 2O_2(g)$$





Kinetic energy → Vibration



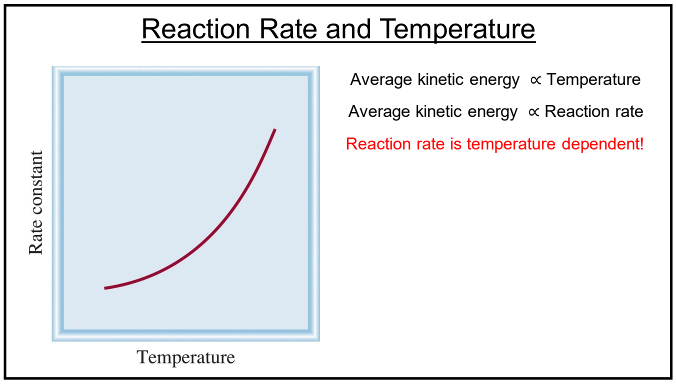
Collision theory of reaction rates

Kinetic energy → Vibration energy

Average kinetic energy ∝ Temperature

Average kinetic energy ∝ Reaction rate

Reaction rate is temperature dependent!

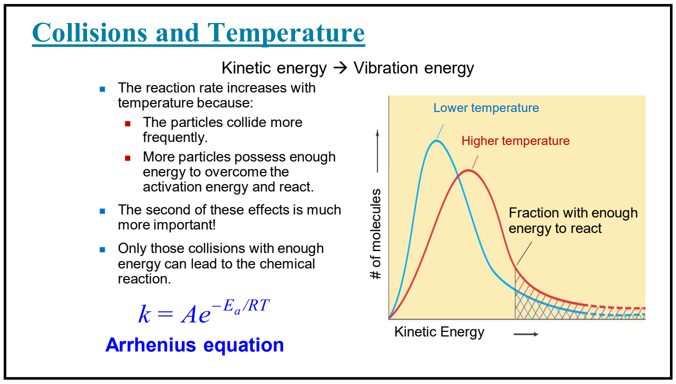


Reaction Rate and Temperature

Average kinetic energy ∝ Temperature

Average kinetic energy ∝ Reaction rate

Reaction rate is temperature dependent!



Collisions and Temperature

Kinetic energy → Vibration energy

- The reaction rate increases with temperature because:
  - The particles collide more frequently.
  - More particles possess enough energy to overcome the activation energy and react.
- The second of these effects is much more important!
- Only those collisions with enough energy can lead to the chemical reaction.

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

Arrhenius equation

Question

Which statement best explains why reaction rates generally increase with increasing temperature?

a. Reaction rates increase with increasing temperature because, as temperature increases, a greater fraction of molecules have enough thermal energy to surmount the activation barrier.

b. Reaction rates increase with increasing temperature because, as temperature increases, the pre-exponential factor of the rate constant increases.

c. Reaction rates increase with increasing temperature because, as temperature increases, molecules decompose into their constituent atoms, which can then form new bonds to form the products.

Answer

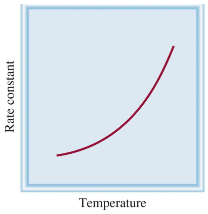
Which statement best explains why reaction rates generally increase with increasing temperature?

a. Reaction rates increase with increasing temperature because, as temperature increases, a greater fraction of molecules have enough thermal energy to surmount the activation barrier.

b. Reaction rates increase with increasing temperature because, as temperature increases, the pre-exponential factor of the rate constant increases.

c. Reaction rates increase with increasing temperature because, as temperature increases, molecules decompose into their constituent atoms, which can then form new bonds to form the products.

Arrhenius Equation



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

E_a is the activation energy (J/mol)

R is the gas constant (8.314 J/K•mol)

T is the absolute temperature (K)

A is the frequency factor (~collision frequency)

Temperature ↑ Rate constant ↑ Reaction rate ↑

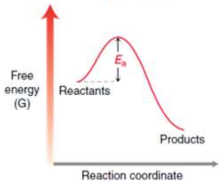
Activation energy ↓ Rate constant ↑ Reaction rate ↑

The rate constant is temperature and E_a dependent!

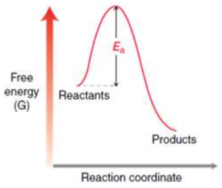
Question

If both are heated to the same temperature, which reaction is faster?

A

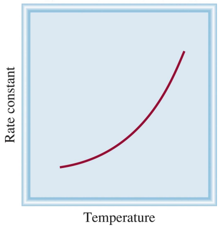


B

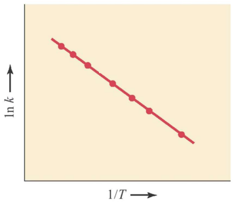


$$k = Ae^{-E_a/RT}$$

Arrhenius Equation



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



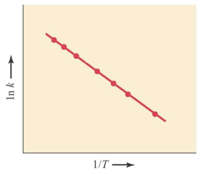
$$y \quad = \quad m \quad \bullet \quad x \quad + \quad b$$

$$\ln k = -\frac{E_a}{R} \bullet \frac{1}{T} + \ln A$$

The activation energy can be determined by plotting the natural log of the rate constant vs. the inverse temperature.

Arrhenius Equation

Alternate Forms of the Arrhenius Equation



Slope = change in y/the change in x

$$m = \frac{y_2 - y_1}{x_2 - x_1}$$

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

or

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

If we know E_a and k_1 at one temperature we can predict k_2 at another T.

If we know k_1 at one temperature and k_2 at another T we can find E_a.

The rate constant of a first-order reaction is 3.46 × 10^{-2} s^{-1} at 298 K.

What is the rate constant at 350 K if the activation energy for the reaction is 50.2 kJ/mol?

$$\ln\frac{k_1}{k_2} = \frac{E_a}{R}\left(\frac{T_1 - T_2}{T_1T_2}\right)$$

$k_1 = 3.46 \times 10^{-2}\ \text{s}^{-1}$ $k_2 = ?$

$T_1 = 298\ \text{K}$ $T_2 = 350\ \text{K}$

E_a = 50.2 kJ/mol

Solution The data are

$k_1 = 3.46 \times 10^{-2}\ \text{s}^{-1}$ $k_2 = ?$

$T_1 = 298\ \text{K}$ $T_2 = 350\ \text{K}$

E_a = 50.2 kJ/mol

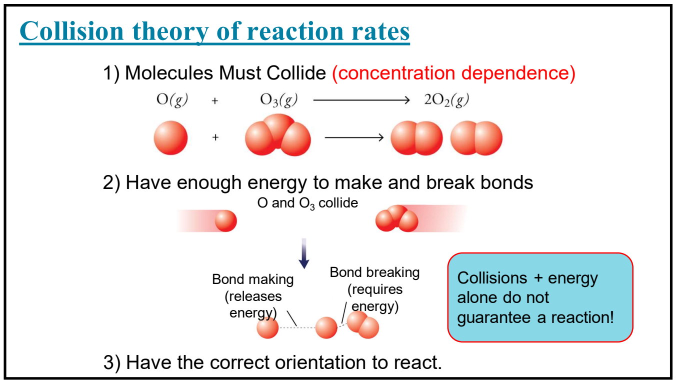
Substituting: $$\ln\frac{k_1}{k_2} = \frac{E_a}{R}\left(\frac{T_1 - T_2}{T_1T_2}\right)$$

$$\ln\frac{3.46 \times 10^{-2}\ \text{s}^{-1}}{k_2} = \frac{50.2 \times 10^3\ \text{J/mol}}{8.314\ \text{J/K} \cdot \text{mol}}\left[\frac{298\ \text{K} - 350\ \text{K}}{(298\ \text{K})(350\ \text{K})}\right]$$

$$\ln\frac{3.46 \times 10^{-2}\ \text{s}^{-1}}{k_2} = -3.01$$

$$\frac{3.46 \times 10^{-2}\ \text{s}^{-1}}{k_2} = e^{-3.01} = 0.0493$$

$$k_2 = 0.702\ \text{s}^{-1}$$



Collision theory of reaction rates

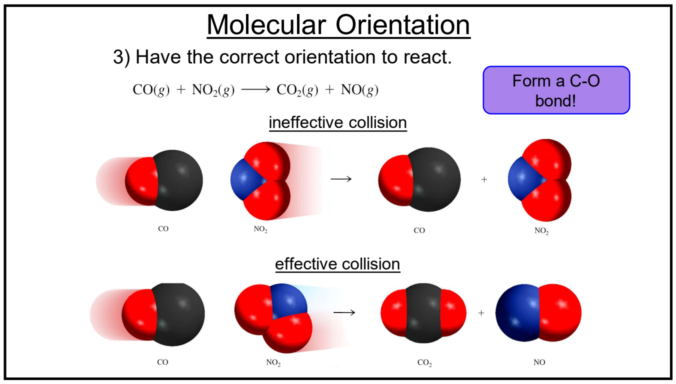
1) Molecules Must Collide (concentration dependence)

$$O(g) + O_3(g) \longrightarrow 2O_2(g)$$

2) Have enough energy to make and break bonds

Collisions + energy alone do not guarantee a reaction!

3) Have the correct orientation to react.



Molecular Orientation

3) Have the correct orientation to react.

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

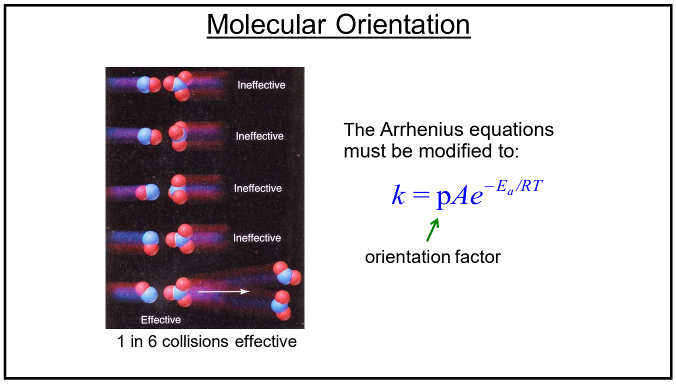
Form a C-O bond!

ineffective collision

effective collision

Orientation Factor (1 of 2)

- The orientation factor, *p*, is a statistical term relating the frequency factor to the collision frequency.
- For most reactions, $p < 1$.
- Generally, the more complex the reactant molecules, the smaller the value of *p*.
- For reactions involving atoms colliding, $p \approx 1$ because of the spherical nature of the atoms.
- Some reactions actually can have a $p > 1$.
  - Generally involve electron transfer



Molecular Orientation

1 in 6 collisions effective

The Arrhenius equations must be modified to:

$$k = \underset{\uparrow}{p}Ae^{-E_a/RT}$$

orientation factor

Question

Which reaction do you expect to have the smallest orientation factor?

a. $H(g) + I(g) \rightarrow HI(g)$

b. $H_2(g) + I_2(g) \rightarrow 2\,HI(g)$

c. $HCl(g) + HCl(g) \rightarrow H_2(g) + Cl_2(g)$

Answer

Which reaction do you expect to have the smallest orientation factor?

a. $\mathbf{H(g) + I(g) \rightarrow HI(g)}$

b. $H_2(g) + I_2(g) \rightarrow 2\,HI(g)$

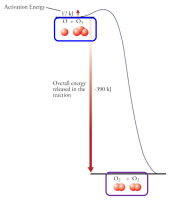
c. $HCl(g) + HCl(g) \rightarrow H_2(g) + Cl_2(g)$

Collision theory of reaction rates

1) Molecules Must Collide (concentration)

2) Have enough energy to make and break bonds (Temp)

3) Have the correct orientation to react.



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

$$\boxed{O(g) + O_3(g)} \longrightarrow \boxed{2O_2(g)}$$

Start

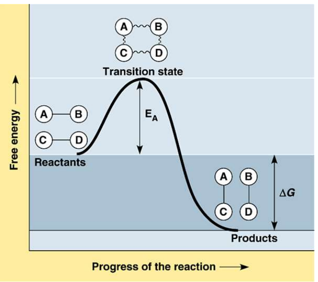
Finish

What about everything in between?

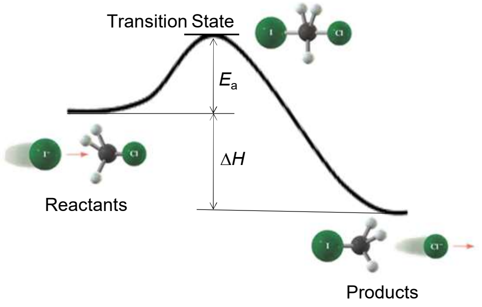
Transition State Theory

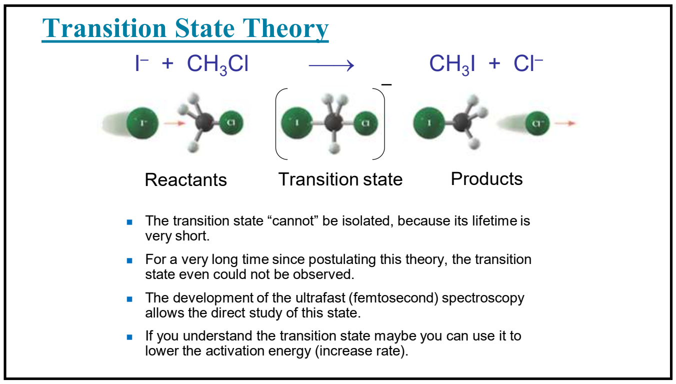
- Postulate of the transition state theory:
  - Reactants form a high energy intermediate, the ***transition state***, which then falls apart into the products.
- For a reaction to occur, the reactants must acquire sufficient energy to form the transition state.
  - This is the ***activation energy*** of the reaction.
- The transition state is neither reactant nor product, but a transitional species with partial bonds.
- To reach the ***transition state***, or ***activated complex***, the energy of colliding particles should be equal to or greater than the activation energy.

Transition State Theory



Transition State Theory



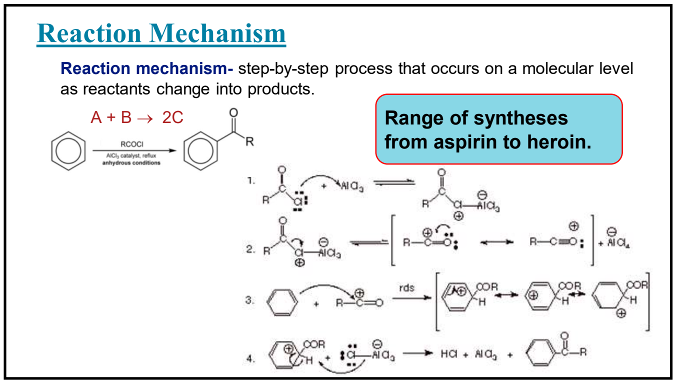


Transition State Theory

$I^- + CH_3Cl \longrightarrow CH_3I + Cl^-$

Reactants Transition state Products

- The transition state “cannot” be isolated, because its lifetime is very short.
- For a very long time since postulating this theory, the transition state even could not be observed.
- The development of the ultrafast (femtosecond) spectroscopy allows the direct study of this state.
- If you understand the transition state maybe you can use it to lower the activation energy (increase rate).

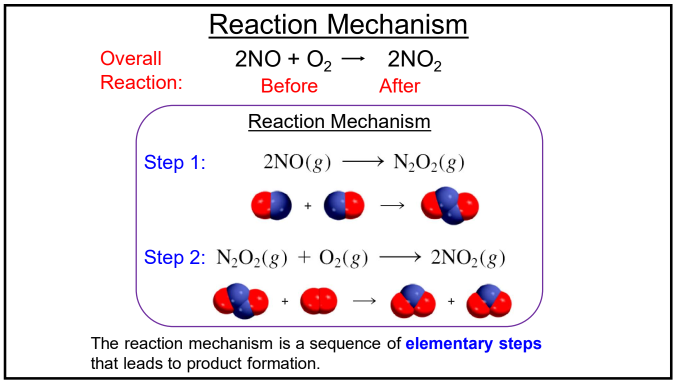


Reaction Mechanism

Reaction mechanism- step-by-step process that occurs on a molecular level as reactants change into products.

A + B → 2C

Range of syntheses from aspirin to heroin.



Reaction Mechanism

Overall Reaction: $2NO + O_2 \longrightarrow 2NO_2$

Before After

Reaction Mechanism

Step 1: $2NO(g) \longrightarrow N_2O_2(g)$

Step 2: $N_2O_2(g) + O_2(g) \longrightarrow 2NO_2(g)$

The reaction mechanism is a sequence of **elementary steps** that leads to product formation.

Reaction Mechanism

A reaction mechanism can have one step or several steps.

Step 1: $2NO(g) \longrightarrow \cancel{N_2O_2(g)}$

Step 2: $\cancel{N_2O_2(g)} + O_2(g) \longrightarrow 2NO_2(g)$

Overall Reaction: $2NO + O_2 \longrightarrow 2NO_2$

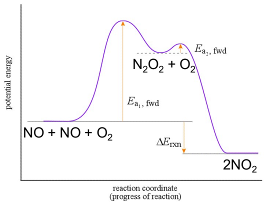
- N_2O_2 is an intermediate because it appears in the mechanism (elementary steps) but not in the overall reaction.
- Reaction intermediates are usually unstable relative to the reactants and/or products.
- They are, however far more stable than transition states.
- Can be detected during the reaction!
- Sometimes stable enough to be isolated.

Reaction Mechanism

Step 1: $2NO(g) \longrightarrow N_2O_2(g)$

Step 2: $N_2O_2(g) + O_2(g) \longrightarrow 2NO_2(g)$

Overall Reaction: $2NO + O_2 \longrightarrow 2NO_2$



- Each elementary step has a valley.
- Reaction intermediates are usually unstable relative to the reactants and/or products.
- They are, however more stable than transition states.
- Sometimes stable enough to be isolated.

Molecularity of a Reaction

The ***molecularity of a reaction*** is the number of molecules reacting in an elementary step.

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

The rate law for an elementary step is written directly from that step.

Step 1: $2NO(g) \longrightarrow N_2O_2(g)$ Bimolecular rate = $k[NO]^2$

Step 2: $N_2O_2(g) + O_2(g) \longrightarrow 2NO_2(g)$ Bimolecular rate = $k[N_2O_2]$ $[NO_2]$

Overall Reaction: $2NO + O_2 \longrightarrow 2NO_2$

Molecularity Example

$CH_4 + Cl_2 \rightarrow HCl + CCl_4 + CH_3Cl\ldots$

Write down the rate laws and describe them as uni- bi- or ter-molecular steps.

Elementary reactions:	Molecularity	Rate Law
$Cl_2 \rightarrow 2\,Cl$	unimolecular	rate = $k[Cl_2]$
$2\,Cl \rightarrow Cl_2$	bimolecular	rate = $k[Cl]^2$
$Cl + CH_4 \rightarrow HCl + CH_3$	bimolecular	rate = $k[Cl][CH_4]$
$CH_3 + Cl \rightarrow CH_3Cl$		
$CH_3 + CH_3 \rightarrow CH_3\text{-}CH_3$		
$CH_3Cl + Cl \rightarrow HCl + CH_2Cl$		
$CH_2Cl + Cl \rightarrow CH_2Cl_2$		
* * * (and more)		

Rate Law of the individual steps, not the overall reaction!

Overall rate law is dictated by the slowest step

Rate Determining Step

The rate determining step is the **slowest** step in the sequence of steps leading to product formation.

Overall rate = rate for slowest step

Overall rate law = rate law for the slowest step

Rate Determining Step Question

$2\,NO_2 + F_2 \rightarrow 2\,NO_2F$

Proposed two-step mechanism:

i $NO_2 + F_2 \rightarrow NO_2F + F$ *rate* = $k\,[NO_2][F_2]$

ii $NO_2 + F \rightarrow NO_2F$ *rate* = $k\,[NO_2][F]$

Are there any intermediates in this reaction?

F

What are the rate laws for each step?

The overall rate law is *rate* = $k\,[NO_2][F_2]$, what is the rate determining step?

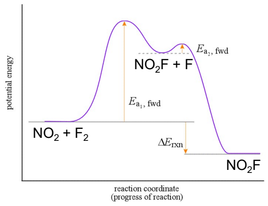
Rate law for each step is related to stoichiometry.
Rate law for the overall reaction is not (must be determined experimentally).

Rate Determining Step

Proposed two-step mechanism:

i $NO_2 + F_2 \rightarrow NO_2F + F$ *Slow Step*

ii $NO_2 + F \rightarrow NO_2F$



Slower step has a higher activation barrier.

The gas-phase decomposition of nitrous oxide (N_2O) is believed to occur via two elementary steps:

$$\text{Step 1:} \quad N_2O \xrightarrow{k_1} N_2 + O$$
$$\text{Step 2:} \quad N_2O + O \xrightarrow{k_2} N_2 + O_2$$

Question:

Experimentally the rate law is found to be rate = $k[N_2O]$.

1) What is the equation for the overall reaction?

A) $2N_2O + O \rightarrow 2N_2 + O + O_2$
B) $N_2O + O \rightarrow N_2 + O + O_2$
C) $2N_2O \rightarrow 2N_2 + O_2$
D) $2N_2O \rightarrow 2N_2 + O$

The gas-phase decomposition of nitrous oxide (N_2O) is believed to occur via two elementary steps:

$$\text{Step 1:} \quad N_2O \xrightarrow{k_1} N_2 + O$$
$$\text{Step 2:} \quad N_2O + O \xrightarrow{k_2} N_2 + O_2$$

Experimentally the rate law is found to be rate = $k[N_2O]$.

Question:

1) What is the equation for the overall reaction?
2) Identify the intermediate.

A) N_2O
B) O
C) N_2
D) There isn't one

The gas-phase decomposition of nitrous oxide (N_2O) is believed to occur via two elementary steps:

$$\text{Step 1:} \quad N_2O \xrightarrow{k_1} N_2 + O$$
$$\text{Step 2:} \quad N_2O + O \xrightarrow{k_2} N_2 + O_2$$

Question:

Experimentally the rate law is found to be rate = $k[N_2O]$.

1) What is the equation for the overall reaction?
2) Identify the intermediate.
3) Which reaction step is faster?

A) Step 1.
B) Step 2.
C) Not enough information.

The gas-phase decomposition of nitrous oxide (N_2O) is believed to occur via two elementary steps:

$$\text{Step 1:} \quad N_2O \xrightarrow{k_1} N_2 + O$$
$$\text{Step 2:} \quad N_2O + O \xrightarrow{k_2} N_2 + O_2$$

Question:

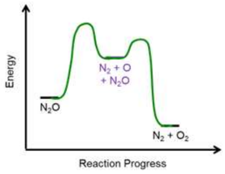
Experimentally the rate law is found to be rate = $k[N_2O]$.

1) What is the equation for the overall reaction?
2) Identify the intermediate.
3) Which reaction step is faster?
4) Propose a reaction coordinate diagram.

The gas-phase decomposition of nitrous oxide (N_2O) is believed to occur via two elementary steps:

$$\text{Step 1:} \quad N_2O \xrightarrow{k_1} N_2 + O$$
$$\text{Step 2:} \quad N_2O + O \xrightarrow{k_2} N_2 + O_2$$

(d) Propose a reaction coordinate diagram.

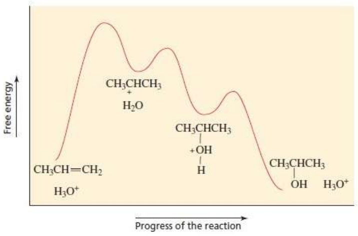


Let's assume it is exothermic.

Intermediate is higher in energy than R and P.

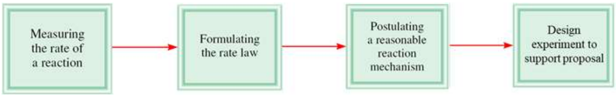
Step 1 slow, higher transition state energy.

Tying it All Together



What is the overall reaction?
Is it exothermic or endothermic?
How many elementary steps?
Write the rate law for each step?
What is the molecularity for each step?
From highest to lowest what are the relative energies of activation?
What is the rate determining step?
What is the overall rate law?
What are the intermediates?
Propose a transition state for each step.

Experimental Kinetics

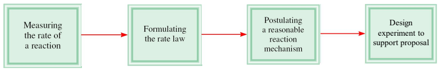


1) Mix reactants together and monitor reaction.
    -Vary concentration of reactants
    -Vary temperature
2) Use data to propose a rate law.
3) Propose a reaction mechanism.
4) Design experiments to support proposal.
    -Attempt to observe/isolate intermediates
    -Labeling experiments
    -Modify structures
5) Try to make it faster/cheaper/more efficient.

3) Propose a reaction mechanism

- Use the concentration dependence and rate law to propose a reaction mechanism.
- The proposed mechanism must meet three criteria:
    - The elementary steps must add up to the overall balanced equation.
    - The mechanism must correlate with the experimentally established rate law.
    - The elementary steps must be physically and chemically reasonable.
    - The mechanism should be as simple as possible while still agreeing with experiment.

Experimental Kinetics



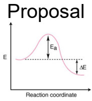
1) Mix reactants together and monitor reaction.
    -Vary concentration of reactants
    -Vary temperature
2) Use data to propose a rate law.
3) Propose a reaction mechanism.
4) Design experiments to support proposal.
    -Attempt to observe/isolate intermediates
    -Labeling experiments
    -Modify structures
5) Try to make it faster/cheaper/more efficient.

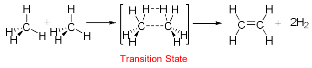
4) Design experiments to support proposal.

-Attempt to observe/isolate intermediates.

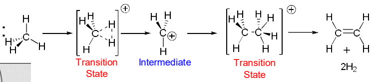
$$2CH_4 \xrightarrow[SbF_5]{FSO_3H} H_2C{=}CH_2 + 2H_2$$

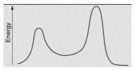
Proposal 1:





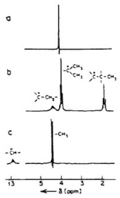
Proposal 2:





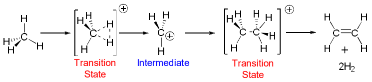
4) Design experiments to support proposal.

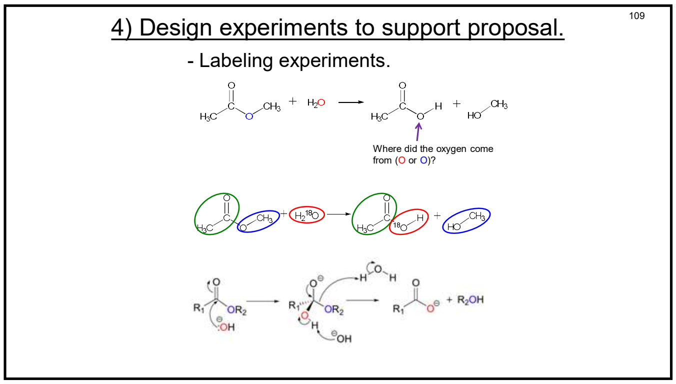
-Attempt to observe/isolate intermediates.



1994 Nobel Prize in chemistry

Proposal 2:

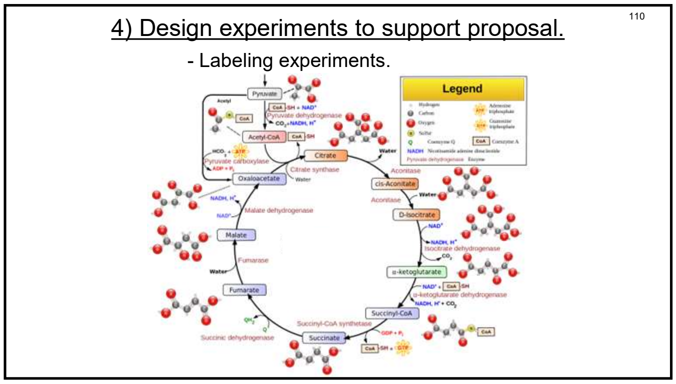




4) Design experiments to support proposal.

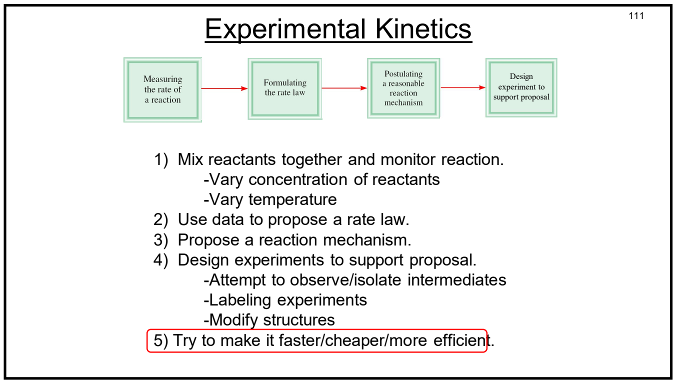
- Labeling experiments.

Where did the oxygen come from (O or O)?



4) Design experiments to support proposal.

- Labeling experiments.



Experimental Kinetics

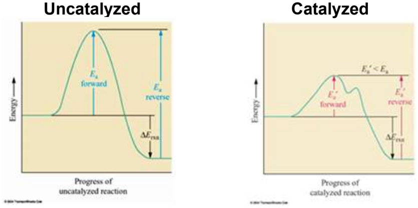
Measuring the rate of a reaction → Formulating the rate law → Postulating a reasonable reaction mechanism → Design experiment to support proposal

1) Mix reactants together and monitor reaction.
    -Vary concentration of reactants
    -Vary temperature
2) Use data to propose a rate law.
3) Propose a reaction mechanism.
4) Design experiments to support proposal.
    -Attempt to observe/isolate intermediates
    -Labeling experiments
    -Modify structures
5) Try to make it faster/cheaper/more efficient.

Catalysis

- ***Catalyst*** is a substance that increases the rate of a chemical reaction without being consumed.
  - Takes part in the reaction (interacts with the reactants).
  - Lowers activation energy by changing the mechanism by which the process occurs.
  - After the interaction it returns to its original state (is not consumed).
  - Speeds up both the forward and the reverse reactions.
  - Does not increase the yield of the product, but gets to the product more quickly.

Catalysis

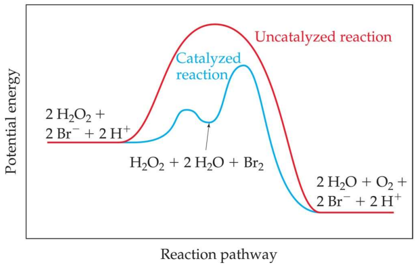


- ΔE and overall reaction are the same.
- Catalyst lowers E_a.

$$k = A \cdot e^{(-E_a/RT)} \qquad E_a\downarrow \quad k\uparrow$$

Catalysis Example

- ΔE and overall reaction are the same.
- Catalyst lowers E_a.
- Catalyst not consumed.



Importance of Catalysis

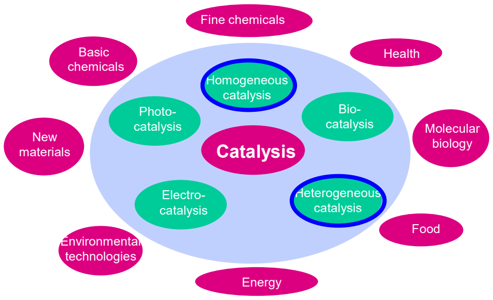
Life on earth

- Catalysts (enzyme) participates most part of life cycle
  e.g. growth, maintenance, decaying
- Converting sun light into various other forms of energies
  e.g. photosynthesis $CO_2 + H_2O \rightarrow H_xC_y + O_2$
- Catalysis plays a key role in our environment

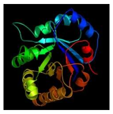
Chemical Industry

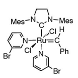
- ca. $2 bn annual sale of catalysts
- ca. $200 bn annual sale of the chemicals that are related products
- 90% of chemical industry has catalysis-related processes
- Catalysts contributes 2% of total investment in a chemical process

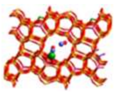
Types of Catalysis


Fine chemicals
Basic chemicals
Health
Homogeneous catalysis
Photo-catalysis
Bio-catalysis
New materials
Catalysis
Molecular biology
Electro-catalysis
Heterogeneous catalysis
Food
Environmental technologies
Energy

Homogeneous vs. Heterogeneous






Zeolite catalyst

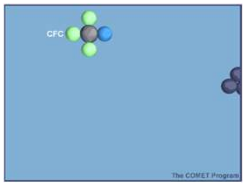

Catalyst powders

Homogeneous catalysis ←
Single phase
(Typically liquid)
Low temperature

→ *Heterogeneous catalysis*
Multiphase
(Mostly solid-liquid and solid-gas)
High temperature

Homogeneous Catalysis: Ozone

Ozone layer- region of Earth's stratosphere that that contains high concentrations of ozone(O_3) and absorbs most of the Sun's UV radiation.



Gas-Gas Reaction

Atmospheric OZONE Equilibrium $O_3 \rightarrow O\bullet + O_2$

CFCs- chlorofluorocarbons CCl_4, CCl_2F_2, CCl_3F…

Reaction process:

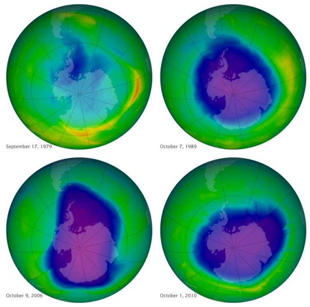
CFC's break down in UV light $CCl_3F \rightarrow Cl\bullet + \bullet CCl_2F$

chlorine radicals then react with ozone $O_3 + Cl\bullet \rightarrow ClO\bullet + O_2$

chlorine radicals are regenerated $ClO\bullet + O \rightarrow O_2 + Cl\bullet$

CFC's are a catalyst. $O_3 \rightarrow O\bullet + O_2$

Homogeneous Catalysis: Ozone



1950s-70s CFCs wide spread use in refrigerators.

1960s and 70s scientists observe a depletion in the ozone layer.

Mid 70s scientists propose a catalytic mechanism for the

$$CCl_2F_2 \rightarrow Cl\bullet + \bullet CClF_2$$

$$O_3 + Cl\bullet \rightarrow ClO\bullet + O_2$$

$$ClO\bullet + O \rightarrow O_2 + Cl\bullet$$

1996- CFC production ends in US and Europe

2010-for the first time in decades the ozone concentration is increasing

---

Homogeneous Catalysis: Enzymes

Enzymes-are biological molecules (proteins) that act as catalysts.

-homogeneous catalysts, reacting in solution (within cells, etc.)

"lock and key" mechanism- molecule specific active site.

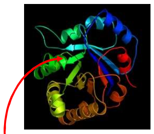
$$A + A \rightarrow B$$

A Only species with the correct shape can enter the active site in the enzyme

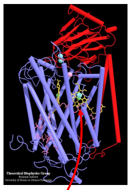
B Once in position, the substrate can react with a lower activation energy

C The new product is released

Homogeneous Catalysis: Enzymes



Triosephosphateisomerase
“TIM”



Cytochrome C Oxidase

Highly tailored “active sites”
Often contain metal atoms

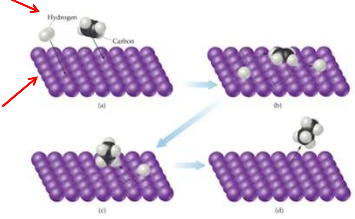
- The “Gold Standard” of catalysts
- Highly specific
- Highly selective
- Highly efficient
- Catalyze very difficult reactions
  - $N_2 \rightarrow NH_3$
  - $CO_2 + H_2O \rightarrow C_6H_{12}O_6$
- “Small scale” reaction

Heterogeneous Catalysis

Catalytic Hydrogenation of Alkenes

Liquid/Gas
Reactants
Products

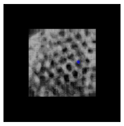
Solid
Catalyst
Surface
Nanoparticle
Zeolite

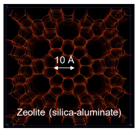


$H_2C{=}CH_2 + 2H_2 \rightarrow C_2H_6$

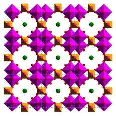
High Surface Area

- Solid phase material
- Porous on the scale of molecular dimensions
  - 10 – 100 Å
  - Up to 1000’s m^2/g surface area
- Catalysis through
  - shape selection
  - acidity/basicity
  - incorporation of metal particles

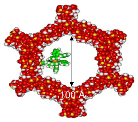




Zeolite (silica-aluminate)



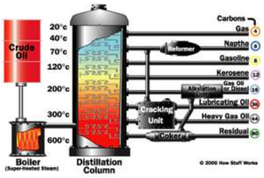
Silico-titanate



MCM-41 (mesoporous silica)

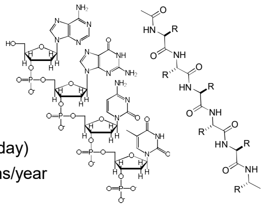
Important Heterogeneous Reactions

- Fischer-Tropsch chemistry
  - $CO + H_2 \rightarrow (CH_2)_n + H_2O$, *syn* gas to liquid fuels
  - Fe/Co catalysts
  - Source of fuel for Axis in WWII
- Fluidized catalytic cracking
  - High MW petroleum → low MW fuels, like gasoline
  - Zeolite catalysts, high temperature combustor
  - In your fuel tank!
- Automotive three-way catalysis
  - $NO_x/CO/HC \rightarrow N_2/H_2O/CO_2/H_2O$
- Haber-Bosch process
  - $N_2 + H_2 \rightarrow NH_3$



Important Heterogeneous Reactions

$$3H_2 + N_2 \rightleftharpoons 2NH_3$$

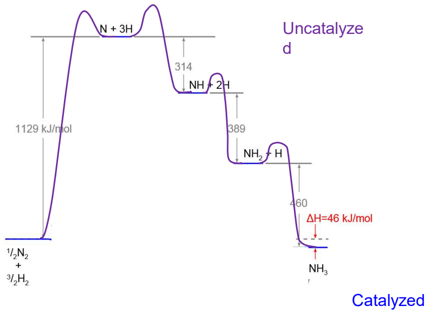


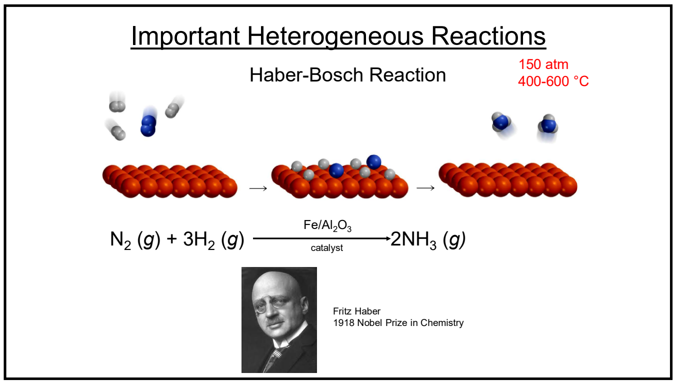
- Fritz Haber (1905)
- Carl Bosch(1909)
  - 80g/hour
- Commercialization (1913)
  - 20 metric tons/day
- Haber - Bosch Process (Today)
  - >100,000,000 metric tons/year

"Arguably the highest impact innovations of the twentieth century: without it, 50% of the world's population would not be here."

Smil, V. *Nature* **1999**, 400, 415.

Important Heterogeneous Reactions





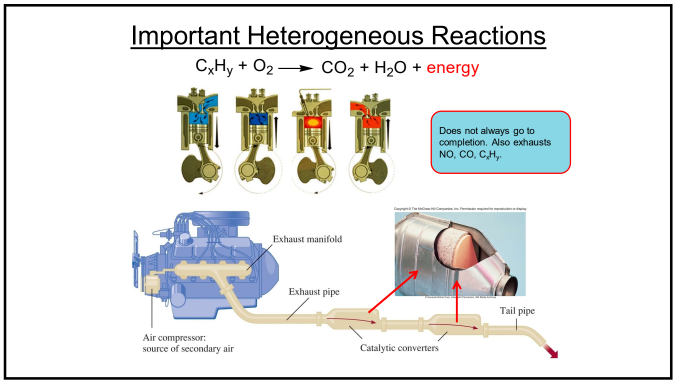
Important Heterogeneous Reactions

Haber-Bosch Reaction

150 atm
400-600 °C

$N_2\ (g) + 3H_2\ (g) \xrightarrow[\text{catalyst}]{Fe/Al_2O_3} 2NH_3\ (g)$

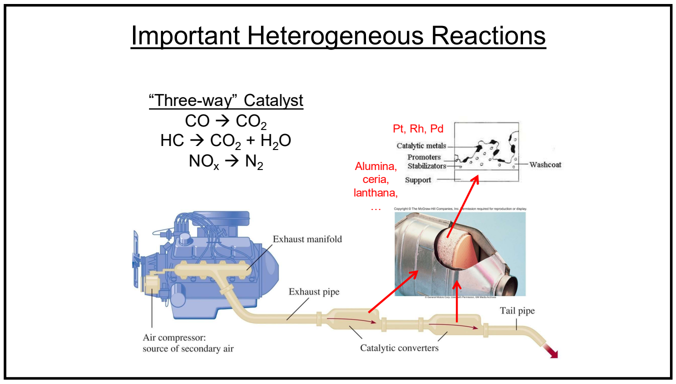
Fritz Haber
1918 Nobel Prize in Chemistry



Important Heterogeneous Reactions

$C_xH_y + O_2 \longrightarrow CO_2 + H_2O + \text{energy}$

Does not always go to completion. Also exhausts NO, CO, C_xH_y.



Important Heterogeneous Reactions

"Three-way" Catalyst

$CO \rightarrow CO_2$

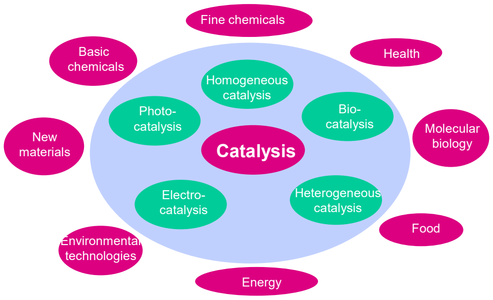
$HC \rightarrow CO_2 + H_2O$

$NO_x \rightarrow N_2$

Pt, Rh, Pd

Alumina, ceria, lanthana, …

Types of Catalysis



Battles still to be won

Future Nobel Prizes:

Make these reactions faster/cheaper/more efficient/room temperature-pressure

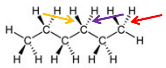
$$N_2 + 3H_2 \longrightarrow 2NH_3$$

$$2CH_4 + O_2 \longrightarrow 2CH_3OH$$

$$2H_2O \longrightarrow O_2 + 2H_2$$

$$2H_2O + CO_2 \longrightarrow 2O_2 + CH_4$$

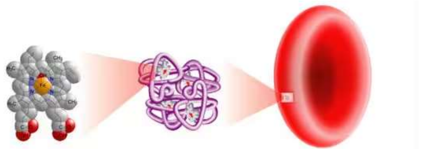
Selective C-H Activation



Question?

Chapter 16

Chemical Equilibrium

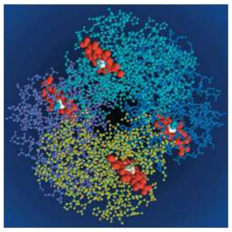


Hemoglobin

- Hemoglobin is a protein (Hb) found in red blood cells that reacts with O_2.
  - It enhances the amount of O_2 that can be carried through the bloodstream.

$$\mathrm{Hb} + \mathrm{O_2} \rightleftharpoons \mathrm{HbO_2}$$

  - The $\rightleftharpoons$ is used to describe a process that is in dynamic equilibrium.



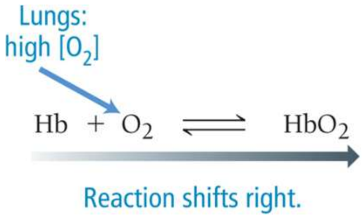
Hemoglobin Equilibrium System

$$\mathbf{Hb + O_2 \rightleftharpoons HbO_2}$$

- The concentrations of Hb, O_2, and HbO_2 are all interdependent.
- The relative amounts of Hb, O_2, and HbO_2 at equilibrium are related to a constant called the **equilibrium constant, *K***.
  - A large value of *K* indicates a high concentration of products at equilibrium.
- Changing the concentration of any one of these necessitates changes to the other concentrations to restore equilibrium.

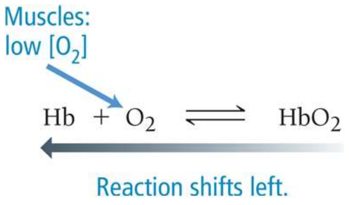
O_2 Transport (1 of 2)

- In the lungs:
  - High concentration of O_2
  - The equilibrium shifts to the right.
  - Hb and O_2 combine to make more HbO_2.



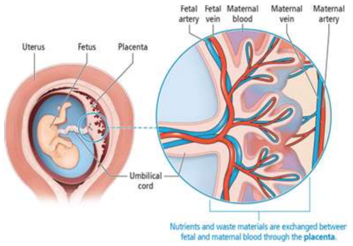
O_2 Transport (2 of 2)

- In the muscles:
  - Low concentration of O_2
  - The equilibrium shifts to the right.
  - HbO_2 breaks down (dissociates), increasing the amount of free O_2.



Fetal Hemoglobin

- Fetal hemoglobin's equilibrium constant is larger than adult hemoglobin's constant.
- Fetal hemoglobin is more efficient at binding O_2.
- O_2 is transferred to the fetal hemoglobin from the mother's hemoglobin in the placenta.



Reaction Dynamics

- When a reaction starts, the reactants are consumed and products are made.
  - The reactant concentrations decrease, and the product concentrations increase.
  - As reactant concentration decreases, the forward reaction rate decreases.
- Eventually, the products can react to re-form some of the reactants, assuming the products are not allowed to escape.
  - As product concentration increases, the reverse reaction rate increases.
- Processes that proceed in both the forward and reverse directions are said to be **reversible**.

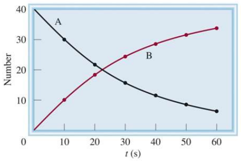
$$\text{reactants} \rightleftharpoons \text{products}$$

Dynamic Processes

Irreversible process:

$A \rightarrow B$

A is converted to B until there is no A and only B.



Reversible process:

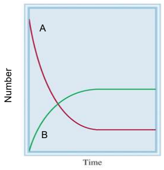
$A \rightarrow B$

$B \rightarrow A$

$A \rightleftharpoons B$

A is in equilibrium with B

Neither A nor B are completely consumed during the reaction.



Dynamic Equilibrium (1 of 3)

- As the forward reaction slows and the reverse reaction accelerates, eventually they reach the same rate.
- **Dynamic equilibrium** is the condition wherein the rates of the forward and reverse reactions are equal.
- Once the reaction reaches equilibrium, the concentrations of all the chemicals remain constant because the chemicals are being consumed and made at the same rate.

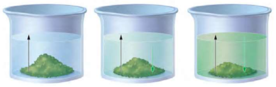
Equilibrium

$A \rightleftharpoons B$

- The change is reversible
- The system is "closed"—no substance can enter or leave
- The system is dynamic - At the macroscopic level, it appears as if nothing is happening, but at the particulate level, reversible changes are occurring continuously.
- Can be at physical equilibrium or chemical equilibrium

Physical Equilibrium- forward and reverse processes occur at the same rate but there is no chemical change.

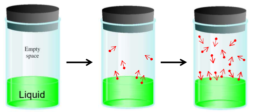
Solubility



At time = 0 At time > 0 At time = ∞

rate of dissolution = rate of precipitation

Vapor Pressure



At time = 0 At time > 0 At time = ∞

rate of vaporization = rate of condensation

Equilibrium

$A \rightleftharpoons B$

- The change is reversible
- The system is "closed"—no substance can enter or leave
- The system is dynamic - At the macroscopic level, it appears as if nothing is happening, but at the particulate level, reversible changes are occurring continuously
- Can be at physical equilibrium or chemical equilibrium

Chemical Equilibrium-

- the rates of the forward and reverse reactions are equal.
- a chemical change is occurring (intramolecular bonds broken/formed)
- concentrations of the reactants and products remain constant.
- this does not mean [conc] of reactants and products are equal!

$N_2O_4\ (g) \rightleftharpoons 2NO_2\ (g)$

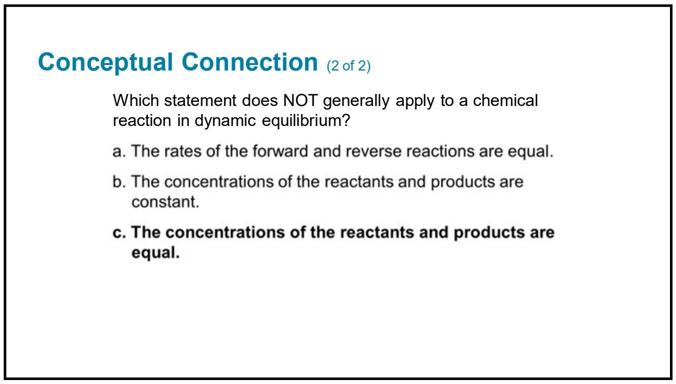
Conceptual Connection (1 of 2)

Which statement does NOT generally apply to a chemical reaction in dynamic equilibrium?

a. The rates of the forward and reverse reactions are equal.

b. The concentrations of the reactants and products are constant.

c. The concentrations of the reactants and products are equal.



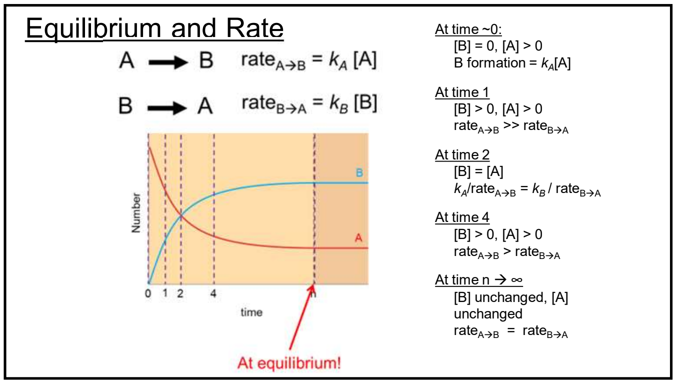
Conceptual Connection (2 of 2)

Which statement does NOT generally apply to a chemical reaction in dynamic equilibrium?

a. The rates of the forward and reverse reactions are equal.

b. The concentrations of the reactants and products are constant.

c. The concentrations of the reactants and products are equal.



Equilibrium and Rate

A → B $\text{rate}_{A \rightarrow B} = k_A\,[A]$

B → A $\text{rate}_{B \rightarrow A} = k_B\,[B]$

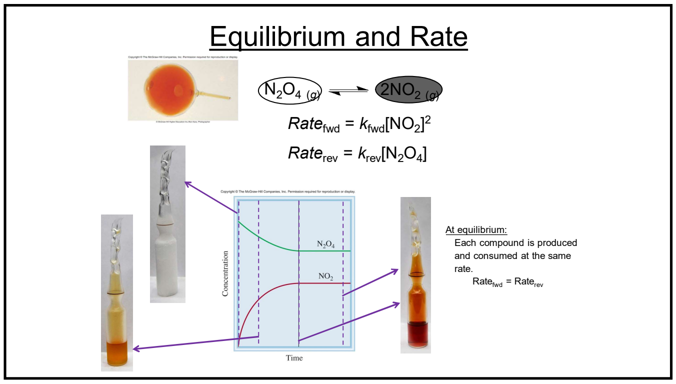
At time ~0:
- $[B] = 0$, $[A] > 0$
- B formation = $k_A[A]$

At time 1
- $[B] > 0$, $[A] > 0$
- $\text{rate}_{A \rightarrow B} >> \text{rate}_{B \rightarrow A}$

At time 2
- $[B] = [A]$
- $k_A/\text{rate}_{A \rightarrow B} = k_B / \text{rate}_{B \rightarrow A}$

At time 4
- $[B] > 0$, $[A] > 0$
- $\text{rate}_{A \rightarrow B} > \text{rate}_{B \rightarrow A}$

At time n → ∞
- [B] unchanged, [A] unchanged
- $\text{rate}_{A \rightarrow B} = \text{rate}_{B \rightarrow A}$



Equilibrium and Rate

$N_2O_4\,(g) \rightleftharpoons 2NO_2\,(g)$

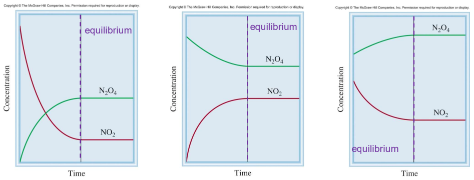
$Rate_{fwd} = k_{fwd}[NO_2]^2$

$Rate_{rev} = k_{rev}[N_2O_4]$

At equilibrium:
Each compound is produced and consumed at the same rate.
$Rate_{fwd} = Rate_{rev}$

Equilibrium and Rate

$N_2O_4\,(g) \rightleftharpoons 2NO_2\,(g)$

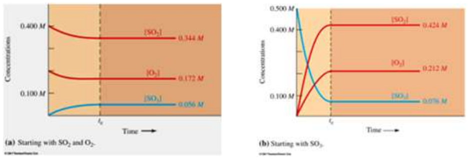


Start with NO_2 Start with N_2O_4 Start with NO_2 & N_2O_4

No matter what concentrations you start with, at some point:
$Rate_{fwd} = Rate_{rev}$
The reaction will reach equilibrium!

Three Species Equilibrium

$$2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$$



No matter what concentrations you start with, at some point:
$Rate_{fwd} = Rate_{rev}$
The reaction will reach equilibrium!

Equilibrium Concentrations

$A \rightleftharpoons B$

- Equilibrium does not mean that concentrations are all equal!!
- However, concentrations at equilibrium are related to the fwd/rev rate constants.
- Every equilibrium has its own equilibrium constant.

At equilibrium:

$rate_{A\to B} = rate_{B\to A}$

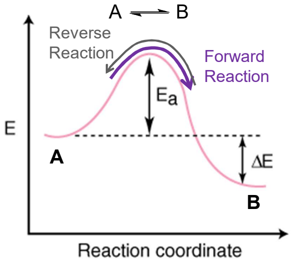
$rate_{A\to B} = k_A\,[A]$
$rate_{B\to A} = k_B\,[B]$

$k_A\,[A] = k_B\,[B]$

Rate constant A→B
Rate constant B→A

$$\frac{k_A}{k_B} = \frac{[B]}{[A]} = K$$

Reaction Diagram



$\frac{k_A}{k_B} = K$

At equilibrium, the number of balls rolling over the hill in each direction is equal.

Equilibrium Constant

For a general reversible reaction such as:

$$aA + bB \rightleftharpoons cC + dD$$

the equilibrium constant is written as

$$K = \frac{[\text{products}]^m}{[\text{reactants}]^n} = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

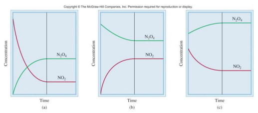
Law of Mass Action

The equilibrium constant for the overall reaction includes stoichiometric coefficients.

General practice is **not** to include units for the equilibrium constant.

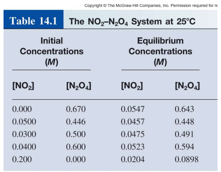
Equilibrium Constant

$$N_2O_{4\,(g)} \rightleftharpoons 2NO_{2\,(g)}$$



Copyright © The McGraw-Hill Companies, Inc. Permission required for reproduction or display.

$K = \frac{[NO_2]^2}{[N_2O_4]}$



Copyright © The McGraw-Hill Companies, Inc. Permission required for re

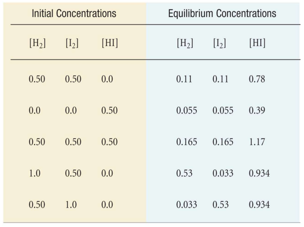
Table 14.1 The NO_2–N_2O_4 System at 25°C

Initial Concentrations (*M*)		Equilibrium Concentrations (*M*)	
$[NO_2]$	$[N_2O_4]$	$[NO_2]$	$[N_2O_4]$
0.000	0.670	0.0547	0.643
0.0500	0.446	0.0457	0.448
0.0300	0.500	0.0475	0.491
0.0400	0.600	0.0523	0.594
0.200	0.000	0.0204	0.0898

$K = 4.6 \times 10^{-3}$

Three Species Equilibrium

$H_2(g) + I_2(g) \rightleftharpoons 2\ HI(g)$

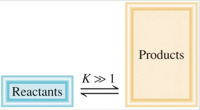


Initial Concentrations			Equilibrium Concentrations		
$[H_2]$	$[I_2]$	$[HI]$	$[H_2]$	$[I_2]$	$[HI]$
0.50	0.50	0.0	0.11	0.11	0.78
0.0	0.0	0.50	0.055	0.055	0.39
0.50	0.50	0.50	0.165	0.165	1.17
1.0	0.50	0.0	0.53	0.033	0.934
0.50	1.0	0.0	0.033	0.53	0.934

No matter how you set up the reaction, the value of the equilibrium constant will be the same if the temperature is the same.

Equilibrium Constant

$a\mathrm{A} + b\mathrm{B} \rightleftharpoons c\mathrm{C} + d\mathrm{D} \qquad K = \frac{[\mathrm{C}]^c[\mathrm{D}]^d}{[\mathrm{A}]^a[\mathrm{B}]^b}$

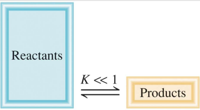


$K >> 1$

Favor product formation

$k_{\mathrm{fwd}} > k_{\mathrm{rev}}$

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



$K << 1$

Favor reactant formation

$k_{\mathrm{fwd}} < k_{\mathrm{rev}}$

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

Equilibrium Constant

A) $4NH_3(g) + 3O_2(g) \Leftrightarrow 2N_2(g) + 6H_2O(g)$ $K = 1\times10^{22}$

B) $N_2(g) + O_2(g) \Leftrightarrow 2NO(g)$ $K = 5\times10^{-31}$

C) $2HF(g) \Leftrightarrow F_2(g) + H_2(g)$ $K = 1\times10^{-13}$

D) $2NOCl(g) \Leftrightarrow 2NO(g) + Cl_2(g)$ $K = 4.7\times10^{-4}$

Question

1) Which reaction most favors the formation of products?

2) Which reaction most favors the formation of reactants?

Equilibrium Constant

For a general reversible reaction such as:

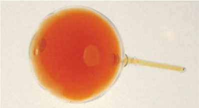
$$aA + bB \rightleftharpoons cC + dD$$

- Equilibrium constants can be expressed using K_c or K_p.
- K_c uses the concentration of reactants and products.

$$K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

- K_p uses the pressure of the gaseous reactants and products.

$$K_p = \frac{P_C{}^c P_D{}^d}{P_A{}^a P_B{}^b}$$



Equilibrium

$$N_2O_{4\,(g)} \rightleftharpoons 2NO_{2\,(g)}$$

In terms of concentration (K_c)

$$K_c = \frac{[NO_2]^2}{[N_2O_4]}$$

In terms of pressure (K_P)

$$K_p = \frac{P_{NO_2}{}^2}{P_{N_2O_4}}$$

$$K_c \neq K_p$$

…at least not always!

K_c vs K_p

$$aA_{(g)} \rightleftharpoons bB_{(g)}$$

$$K_P = \frac{P_B^b}{P_A^a} \qquad K_c = \frac{[B]^b}{[A]^a}$$

Substitution

$$P_AV = n_ART$$

$$P_A = \frac{n_ART}{V}$$

$$K_P = \frac{\left(\frac{n_BRT}{V}\right)^b}{\left(\frac{n_ART}{V}\right)^a} = \frac{\left(\frac{n_B}{V}\right)^b}{\left(\frac{n_A}{V}\right)^a}(RT)^{b-a} \longrightarrow K_P = \frac{[B]^b}{[A]^a}(RT)^{\Delta n}$$

$$\boxed{K_P = K_c(RT)^{\Delta n}}$$

$$\Delta n = b - a$$

= moles of gaseous products − moles of gaseous reactants

K_c vs K_p

$$aA + bB \rightleftharpoons cC + dD$$

$$K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b} \qquad K_p = \frac{P_C{}^c P_D{}^d}{P_A{}^a P_B{}^b}$$

$$K_p = K_c(RT)^{\Delta n}$$

Δn = moles of gaseous products – moles of gaseous reactants

$$\Delta n = (c + d) - (a + b)$$

When does K_p equal K_c?

Equilibria: Phases Matter

Homogenous equilibrium- all reacting species **are in the same phase.**

gas – gas
liquid-liquid
liquid-aqueous

Heterogeneous equilibrium- reacting species **are in different phases.**

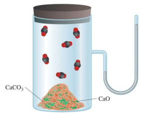
gas – liquid
liquid-solid
solid-gas

$$N_2O_{4\,(g)} \rightleftharpoons 2NO_{2\,(g)}$$

$$CaCO_{3\,(s)} \rightleftharpoons CaO_{(s)} + CO_{2(g)}$$

Copyright © The McGraw-Hill Companies, Inc. Permission required for reproduction or display.

© McGraw-Hill Higher Education Inc./Ken Karp, Photographer



Homogenous Equilibria

-all reacting species **are in the same phase.**

gas-gas equilibria

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

$$K_c = \frac{[HI]^2}{[H_2][I_2]} \qquad K_p = \frac{(HI)^2}{(H_2)(I_2)}$$

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$$

$$K_c = \frac{[NH_2]^2}{[N_2][H_2]^3} \qquad K_p = \frac{P_{NH3}{}^2}{P_{N2}P_{H2}{}^3}$$

H_2O is often used as a solvent(l). However, if H_2O is written as a <u>gas (g)</u>, then its concentration must be considered in K_c and K_p.

$$CH_{4(g)} + 3H_2O_{(g)} \rightleftharpoons CO_{(g)} + 3H_{2(g)}$$

$$K_c = \frac{[CO][H_2]^2}{[CH_4][H_2O]^3} \qquad K_p = \frac{P_{CO}P_H{}^2}{P_{CH4}P_{H2O}{}^3}$$

Homogenous Equilibria

-all reacting species **are in the same phase.**

liquid equilibrium

$$CH_3COOH_{(aq)} + H_2O_{(l)} \rightleftharpoons CH_3COO^-_{(aq)} + H_3O^+_{(aq)}$$

$$K_c = \frac{[CH_3COO^-][H_3O^+]}{[CH_3COOH][H_2O]}$$

$[H_2O]$ = solvent
$[H_2O]$ = constant

The concentration of **pure liquids** are not included in the expression for the equilibrium constant.

$$K_c = \frac{[CH_3COO^-][H_3O^+]}{[CH_3COOH]}$$

Question

Write expressions for the following reversible reactions at equilibrium:

1) $HF_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + F^-_{(aq)}$

A) $K_c = \frac{[H_3O^+][F^-]}{[HF][H_2O]}$ B) $K_c = \frac{[HF]}{[F^-][H_3O^+]}$ C) $K_c = \frac{[F^-][H_3O^+]}{[HF]}$

2) $2NO_{(g)} + O_{2(g)} \rightleftharpoons 2NO_{2(g)}$

A) $K_c = \frac{[NO_2]^2}{[O_2][NO]^2}$ B) $K_c = \frac{[NO_2]}{[O_2][NO]}$ C) $K_P = \frac{P_{NO2}{}^2}{P_{O2}\,P_{NO}{}^2}$

3) $CH_3COOH_{(aq)} + C_2H_5OH_{(aq)} \rightleftharpoons CH_3COOC_2H_{5(aq)} + H_2O_{(l)}$

A) $K_c = \frac{[CH_3COOC_2H_5][H_2O]}{[CH_3COOH][C_2H_5OH]}$ B) $K_c = \frac{[CH_3COOC_2H_5]}{[CH_3COOH][C_2H_5OH]}$

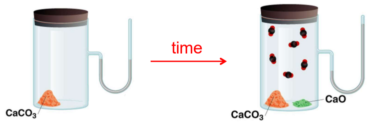
Heterogeneous Equilibria

-reacting species **are in different phases.**

- Can include liquids, gases and solids as either reactants or products.

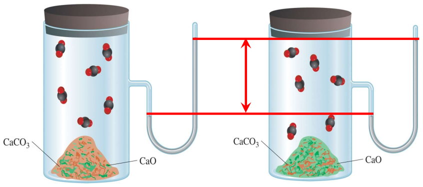
$$CaCO_{3\ (s)} \rightleftharpoons CaO_{\ (s)} + CO_{2\ (g)}$$

Note CaO will not form a neat separated pile!



Heterogenous Equilibria

$CaCO_{3\ (s)} \rightleftharpoons CaO_{\ (s)} + CO_{2\ (g)}$


$CaCO_3 > CaO$ $CaCO_3 < CaO$

P_{CO2} or $[CO_2]$ does not depend on the amount of $CaCO_3$ or CaO

$K_p = P_{CO2}$

Heterogenous Equilibria

$CaCO_{3\ (s)} \rightleftharpoons CaO_{\ (s)} + CO_{2\ (g)}$

$$K_c = \frac{[CaO][CO_2]}{[CaCO_3]}$$

Activity- is a measure of the “effective concentration” of a species in a mixture.

Activity of a solid = 1

$$K_c = \frac{[1][CO_2]}{[1]}$$

$K_c = [CO_2]$ $K_p = P_{CO_2}$

The concentration of **solids** are not included in the expression for the equilibrium constant.

Consider the following heterogeneous equilibrium:

$CaCO_{3(s)} \rightleftharpoons CaO_{(s)} + CO_{2(g)}$

At 800°C, the pressure of CO_2 is 0.236 atm. Calculate:

(a) K_P

Given T and P_{CO2} Find K_p

$K_p = P_{CO_2}$ $K_P = 0.236$

(b) K_c

Have T and K_p Find K_c

$K_p = K_c(RT)^{\Delta n}$

$R = 0.0821$ L atm/K mol $T = 273 + 800 = 1073$ K $\Delta n = 1 - 0 = 1$

$0.236 = K_c(0.0821 \times 1073)^1$

$K_c = 2.68 \times 10^{-3}$

Liquids and Solids

The concentration of **pure liquids** are not included in the expression for the equilibrium constant.

$$CH_3COOH_{(aq)} + H_2O_{(l)} \rightleftharpoons CH_3COO^-_{(aq)} + H_3O^+_{(aq)}$$

$$K_c = \frac{[CH_3COO^-][H_3O^+]}{[CH_3COOH]}$$

The concentration of **solids** are not included in the expression for the equilibrium constant.

$$CaCO_{3\,(s)} \rightleftharpoons CaO_{(s)} + CO_{2\,(g)}$$

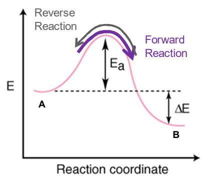
$K_c = [CO_2]$ $K_p = P_{CO_2}$

Writing Equilibrium Constant Expressions

1. The concentrations of the reacting species in the condensed phase are expressed in *M*. In the gaseous phase, the concentrations can be expressed in *M* or in atm.
2. The concentrations of pure solids, pure liquids and solvents do not appear in the equilibrium constant expressions.
3. The equilibrium constant is a dimensionless quantity.
4. In quoting a value for the equilibrium constant, you must specify the balanced equation and the temperature.

Multiple Equilibria

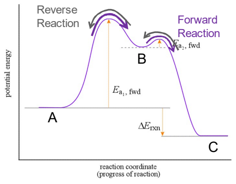
$A \rightleftharpoons B$



Step 1: $A \rightleftharpoons B$

Step 2: $B \rightleftharpoons C$

Overall Reaction: $A \rightleftharpoons C$



$$\frac{k_{A\to B}}{k_{B\to A}} = K$$

$$\frac{k_{A\to B}}{k_{B\to A}} = K_1 \qquad \frac{k_{B\to C}}{k_{C\to B}} = K_2$$

Multiple Equilibria

- –A reaction can be an individual reaction step or a multistep reaction.
- –If the overall reaction is the sum of two or more reactions, the overall reaction Equilibrium Constant is the product of the Equilibrium Constants for the steps

$$\mathbf{K_{overall} = K_1 \times K_2 \times K_3 \times ....}$$

Multiple Equilibria

Product molecules of one equilibrium constant are involved in a second equilibrium process.

$$\begin{array}{lll} A + B \rightleftharpoons \cancel{C} + D & K_c' & K_c' = \dfrac{[C][D]}{[A][B]} \\ \cancel{C} + D \rightleftharpoons E + F & K_c'' & K_c'' = \dfrac{[E][F]}{[C][D]} \\ \hline A + B \rightleftharpoons E + F & K_c & \end{array}$$

$$K_c = K_c' \times K_c'' = \frac{[C][D]}{[A][B]} \times \frac{[E][F]}{[C][D]} \qquad K_c = \frac{[E][F]}{[A][B]}$$

If a reaction can be expressed as the sum of two or more reactions, the equilibrium constant for the overall reaction is given by the product of the equilibrium constants of the individual reactions.

Practice Problem

Determine the overall equilibrium constant for the reaction between Nitrogen & Oxygen to form the toxic gas Nitrogen Dioxide – a component of atmospheric smog

$$\begin{array}{lcccccl} & N_2(g) & + & O_2(g) & \leftrightarrows & 2\cancel{NO}(g) & K_{c1} \\ & 2\cancel{NO}(g) & + & O_2(g) & \leftrightarrows & 2NO_2(g) & K_{c2} \\ \hline \text{Overall:} & N_2(g) & + & 2O_2(g) & \leftrightarrows & 2NO_2(g) & \end{array}$$

$$K_{c1} = \frac{[NO]^2}{[N_2][O_2]} \qquad K_{c2} = \frac{[NO_2]^2}{[NO]^2][O_2]}$$

$$Kc_{overall} = K_{c1} \times K_{c2} = \frac{[NO]^2}{[N_2][O_2]} \times \frac{[NO_2]^2}{[NO]^2[O_2]} = \frac{[NO_2]^2}{[N_2][O_2]^2}$$

Multiple Equilibria

Overall Equilibrium: $H_2CO_3(aq) \rightleftharpoons 2H^+(aq) + CO_3^{2-}(aq)$ K_c

Equilibrium 1: $H_2CO_3(aq) \rightleftharpoons H^+(aq) + HCO_3^-(aq)$ K'_c

Equilibrium 2: $HCO_3^-(aq) \rightleftharpoons H^+(aq) + CO_3^{2-}(aq)$ K''_c

Given K'_c and K''_c what is K_c?

$$K_c = K'_c K''_c = \frac{[H^+]\cancel{[HCO_3^-]}}{[H_2CO_3]} \times \frac{[H^+][CO_3^{2-}]}{\cancel{[HCO_3^-]}}$$

$$K_c = \frac{[H^+]^2[CO_3^{2-}]}{[H_2CO_3]}$$

$$K_c = K'_c K''_c$$

Rules for Manipulating K

- The overall reaction equilibrium constant (K) is the product of the equilibrium constants for the steps.

$$K_{overall} = K_1 \times K_2 \times K_3 \times ....$$

- If the equation is reversed, the equilibrium constant is inverted.

$$A + 2B \leftrightarrow 3C \qquad K_{forward} = \frac{[C]^3}{[A][B]^2}$$

$$3C \leftrightarrow A + 2B \qquad K_{reverse} = \frac{[A][B]^2}{[C]^3} = \frac{1}{K_{forward}}$$

- If the equation is multiplied by a factor, the equilibrium constant is raised to the same factor.

Writing Equilibrium Constant Expressions

1. The concentrations of the reacting species in the condensed phase are expressed in *M* (K_c). In the gaseous phase, the concentrations can be expressed in *M* (K_c) or in atm (K_p).
2. The concentrations of pure solids, pure liquids and solvents **DO NOT** appear in the equilibrium constant expressions.
3. The equilibrium constant is a dimensionless quantity.
4. In quoting a value for the equilibrium constant, you must specify the balanced equation and the temperature.
5. If a reaction can be expressed as a sum of two or more reactions, the equilibrium constant for the **overall reaction is given by the product of the equilibrium constants of the individual reactions**.

Equilibrium Constant

For a general reversible reaction such as:

$$aA + bB \rightleftharpoons cC + dD$$

- Equilibrium constants can be expressed using K_c or K_p.
- K_c uses the concentration of reactants and products.

$$K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

- K_p uses the pressure of the gaseous reactants and products.

$$K_p = \frac{P_C^{\,c}\, P_D^{\,d}}{P_A^{\,a}\, P_B^{\,b}}$$

I have *K*, now what?

I have *K*, now what?

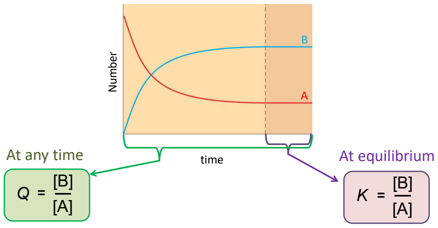
We can:

- Predict the direction in which a reaction mixture will proceed to reach equilibrium.
- Calculate the concentration of reactants and products once equilibrium has been reached.
- Predict if and which direction the equilibrium will shift upon perturbation.

Reaction Quotient

Reaction Quotient- is a function of the concentrations or pressures of the chemical species involved in a chemical reaction.

$$A \rightleftharpoons B$$



At any time

$$Q = \frac{[B]}{[A]}$$

At equilibrium

$$K = \frac{[B]}{[A]}$$

Reaction Quotient

- The **reaction quotient** $\boldsymbol{Q}$ has the same form as the equilibrium constant $\boldsymbol{K}$
- The major difference between $\boldsymbol{Q}$ and $\boldsymbol{K}$ is that the concentrations used in $\boldsymbol{Q}$ are ***not necessarily equilibrium values.***

$$aA + bB \rightleftharpoons cC + dD$$

$$Q = \frac{[\text{products}]^m}{[\text{reactants}]^n} = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

Q can be calculated at any time!

Reaction Quotient

- Why do we need Q if it does not use equilibrium concentrations?
- The reaction quotient will help us predict how the equilibrium will respond to an applied stress:

$$aA + bB \rightleftharpoons cC + dD$$

$Q = K_c$: the system is at equilibrium

$Q < K_c$: the reaction proceeds to the right

$Q > K_c$: the reaction proceeds to the left

Reaction Quotient

$$aA + bB \rightleftharpoons cC + dD$$

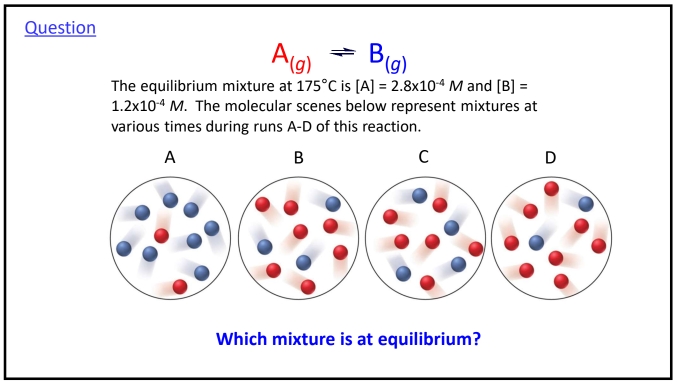
$$Q = \frac{[C]^c\,[D]^d}{[A]^a\,[B]^b} \qquad K = \frac{[C]^c\,[D]^d}{[A]^a\,[B]^b}$$

$Q = K_c$: the system is at equilibrium
concentration of reactants and products stays the same

$Q < K_c$: the reaction proceeds to the right
generate more products, consume more reactant

$Q > K_c$: the reaction proceeds to the left
consume more products, generate more reactant

Can predict which way will it shift.

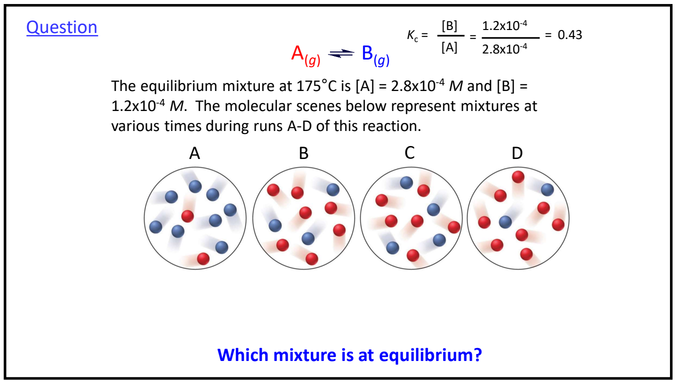


Question

$A_{(g)} \rightleftharpoons B_{(g)}$

The equilibrium mixture at 175°C is [A] = $2.8\text{x}10^{-4}$ *M* and [B] = $1.2\text{x}10^{-4}$ *M*. The molecular scenes below represent mixtures at various times during runs A-D of this reaction.

Which mixture is at equilibrium?



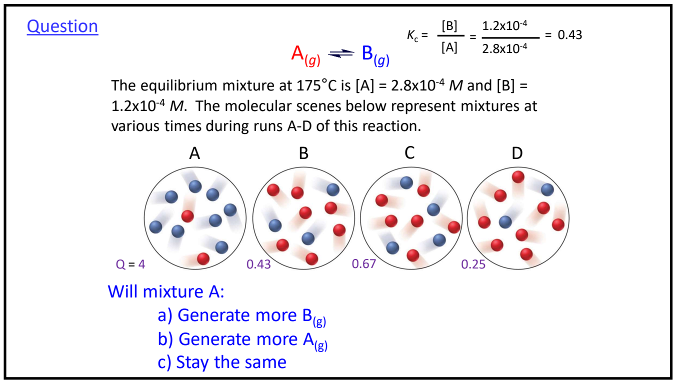
Question

$K_c = \frac{[B]}{[A]} = \frac{1.2\text{x}10^{-4}}{2.8\text{x}10^{-4}} = 0.43$

$A_{(g)} \rightleftharpoons B_{(g)}$

The equilibrium mixture at 175°C is [A] = $2.8\text{x}10^{-4}$ *M* and [B] = $1.2\text{x}10^{-4}$ *M*. The molecular scenes below represent mixtures at various times during runs A-D of this reaction.

Which mixture is at equilibrium?



Question

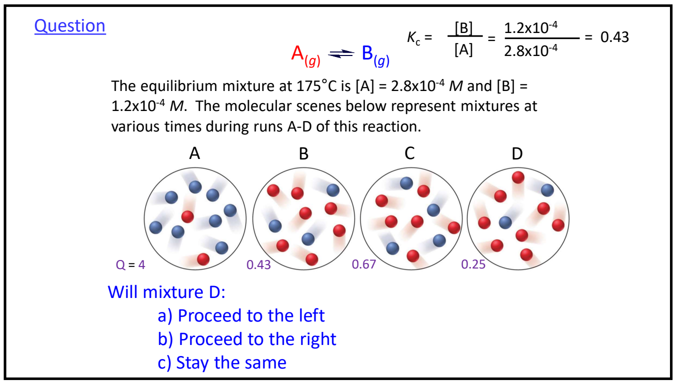
$K_c = \frac{[B]}{[A]} = \frac{1.2\text{x}10^{-4}}{2.8\text{x}10^{-4}} = 0.43$

$A_{(g)} \rightleftharpoons B_{(g)}$

The equilibrium mixture at 175°C is [A] = $2.8\text{x}10^{-4}$ *M* and [B] = $1.2\text{x}10^{-4}$ *M*. The molecular scenes below represent mixtures at various times during runs A-D of this reaction.

Will mixture A:

a) Generate more $B_{(g)}$
b) Generate more $A_{(g)}$
c) Stay the same



Question

$A_{(g)} \rightleftharpoons B_{(g)}$

$K_c = \frac{[B]}{[A]} = \frac{1.2\text{x}10^{-4}}{2.8\text{x}10^{-4}} = 0.43$

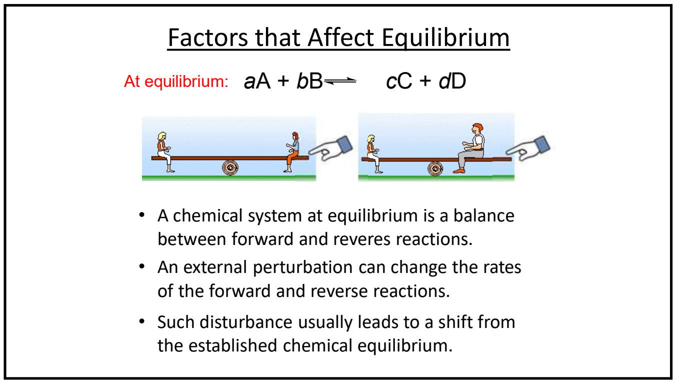
The equilibrium mixture at 175°C is [A] = 2.8x10^{-4} *M* and [B] = 1.2x10^{-4} *M*. The molecular scenes below represent mixtures at various times during runs A-D of this reaction.

Will mixture D:

a) Proceed to the left

b) Proceed to the right

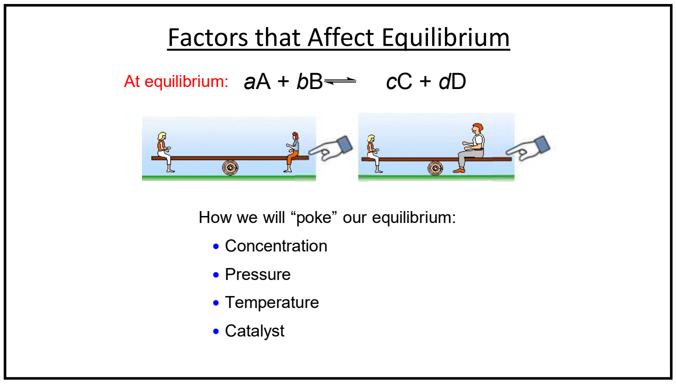
c) Stay the same



Factors that Affect Equilibrium

At equilibrium: $aA + bB \rightleftharpoons cC + dD$

- A chemical system at equilibrium is a balance between forward and reveres reactions.
- An external perturbation can change the rates of the forward and reverse reactions.
- Such disturbance usually leads to a shift from the established chemical equilibrium.



Factors that Affect Equilibrium

At equilibrium: $aA + bB \rightleftharpoons cC + dD$

How we will “poke” our equilibrium:

- Concentration
- Pressure
- Temperature
- Catalyst

Le Châtelier's Principle

When a chemical system at equilibrium is disturbed, it returns to equilibrium by undergoing a *net reaction* that *reduces* the effect of the disturbance.

1) The system is at equilibrium.
2) We poke/stress/disturb the system.
3) The system is no longer at equilibrium.
4) LCP says system will react and return to equilibrium.

Henry Le Châtelier
(1850-1936)

Change in Concentrations

$$aA + bB \rightleftharpoons cC + dD$$

1) The system is at equilibrium.

$$K = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

2) We poke/stress/disturb the system.
double the concentration of D

3) The system is no longer at equilibrium.

$$Q = \frac{[C]^c[2D]^d}{[A]^a[B]^b}$$

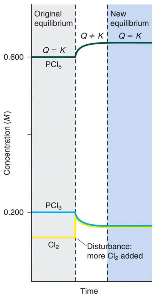
4) LCP says system will react and return to equilibrium. $Q > K$ The reaction will "shift left"

Change in Concentrations

$$PCl_{3(g)} + Cl_{2(g)} \rightleftharpoons PCl_{5(g)}$$

$$K = \frac{P_{PCl5}}{P_{PCl3}\,P_{Cl2}}$$

1) The system is at equilibrium.
$Q = K$
2) We add $Cl_{2(g)}$.
3) The system is no longer at equilibrium.
$Q < K$
4) LCP says system will react and return to equilibrium ($Q = K$).
↓ PCl_3 ↓ Cl_2 ↑ PCl_5



A change in conc has *no effect* on the value of *K*!

Change in Concentrations

$$aA + bB \rightleftharpoons cC + dD$$

$$K = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

Change	**Shifts the Equilibrium**
Add [products]	left
Remove [products]	right
Add [reactants]	right
Remove [reactants]	left

To reach equilibrium again:

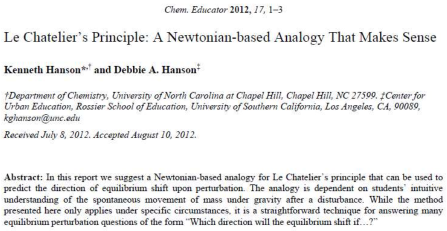
Left Shift: decrease in [products], increase in [reactants]

Right Shift: decrease in [reactants], increase in [products]

Change in Concentrations

Rather than memorize the rules or calculate Q every time,
I propose an alternative strategy:

The Hanson method



Chem. Educator **2012,** *17,* 1–3

Le Chatelier's Principle: A Newtonian-based Analogy That Makes Sense

Kenneth Hanson*,† and Debbie A. Hanson‡

†Department of Chemistry, University of North Carolina at Chapel Hill, Chapel Hill, NC 27599. ‡Center for Urban Education, Rossier School of Education, University of Southern California, Los Angeles, CA, 90089, kghanson@unc.edu

Received July 8, 2012. Accepted August 10, 2012.

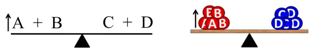
Abstract: In this report we suggest a Newtonian-based analogy for Le Chatelier's principle that can be used to predict the direction of equilibrium shift upon perturbation. The analogy is dependent on students' intuitive understanding of the spontaneous movement of mass under gravity after a disturbance. While the method presented here only applies under specific circumstances, it is a straightforward technique for answering many equilibrium perturbation questions of the form "Which direction will the equilibrium shift if…?"

Change in Concentrations

$$A + B \rightleftharpoons C + D$$

Step 1: Visualize or draw the equilibrium as a see-saw with the fulcrum under the equilibrium arrow.

Step 2: Which ever component is being added (removed), visualize an up (down) arrow attached to that side of the see-saw. For addition of A:



Step 3: Which ever component is being added (removed), visualize an up (down) arrow attached to that side of the see-saw. For addition of A:

Reaction shifts right!

Example Problem

$FeSCN^{2+}_{(aq)} \rightleftharpoons Fe^{3+}_{(aq)} + SCN^{-}_{(aq)}$

red yellow

Which way does the reaction shift if:

we add NaSCN?

↑

$FeSCN^{2+}_{(aq)} \rightleftharpoons Fe^{3+}_{(aq)} + SCN^{-}_{(aq)}$

we add $C_2O_4^{2-}$ ($Fe^{3+} + C_2O_4^{2-} \rightarrow Fe(C_2O_4)_3^{3-}$)?

$FeSCN^{2+}_{(aq)} \rightleftharpoons Fe^{3+}_{(aq)} + SCN^{-}_{(aq)}$

↓

we add $Fe(NO_3)_3$? ↑

$FeSCN^{2+}_{(aq)} \rightleftharpoons Fe^{3+}_{(aq)} + SCN^{-}_{(aq)}$

Change in Concentrations

$K_p = \frac{P_{CO_2}}{P_{O_2}}$

$C_{(s)} + O_{2(g)} \rightleftharpoons CO_{2(g)}$

Question:

Will doubling O_2:

a) Shift right
b) Shift left
c) Stay the same

Change in Concentrations

$K_p = \frac{P_{CO_2}}{P_{O_2}}$

$C_{(s)} + O_{2(g)} \rightleftharpoons CO_{2(g)}$

Question:

Will doubling $C_{(s)}$:

a) Shift right
b) Shift left
c) Stay the same

Question

To improve air quality and obtain a useful product, chemists often remove sulfur from coal and natural gas by treating the contaminant hydrogen sulfide with O_2:

$$2H_2S_{(g)} + O_{2(g)} \rightleftharpoons 2S_{(s)} + 2H_2O_{(g)}$$

What happens to:

(1) $[H_2O]$ if O_2 is added?
- a) increase
- b) decrease
- c) stay the same

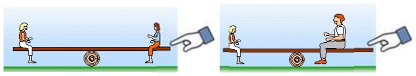
(2) $[H_2S]$ if O_2 is added?
- a) increase
- b) decrease
- c) stay the same

(3) $[O_2]$ if H_2S is removed?
- a) increase
- b) decrease
- c) stay the same

(4) $[H_2S]$ if sulfur is added?
- a) increase
- b) decrease
- c) stay the same

Factors that Affect Equilibrium

At equilibrium: $aA + bB \rightleftharpoons cC + dD$



How we will "poke" our equilibrium:

- Concentration ✓
- Pressure
- Temperature
- Catalyst

Change in Pressure

$$A_{(g)} + B_{(g)} \rightleftharpoons C_{(g)}$$

We can change pressure in a reaction vessel three different ways:

1) Add A, B or C

Changing the concentration of a gaseous component causes the equilibrium to shift according to LCP.

2) Increasing or decreasing the volume of the chamber.

3) Adding an inert gas (a gas not involved in the rxn).

Changes in pressure (volume) have ***no effect*** on the value of *K*.

2) Change in Volume

$$A_{(g)} + B_{(g)} \rightleftharpoons C_{(g)}$$

- Changing the volume/pressure of a reaction will have little influence on liquid, aqueous or solid species.
- Concentration of gases are greatly affected by pressure and volume changes according to the ideal gas law.

$$PV = nRT \qquad P \propto 1/V$$
$$P = (n/V)RT$$

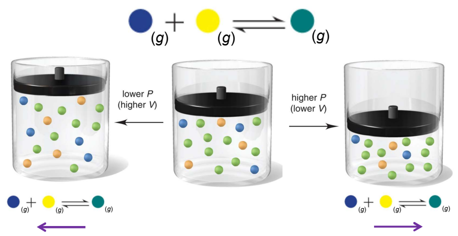
- Increasing pressure (or reducing volume) effectively increase the concentration of gasses.

2) Change in Volume

$$A_{(g)} + B_{(g)} \rightleftharpoons C_{(g)}$$

- When the pressure is increased (or volume is decreased), the reaction proceeds to decrease the total amount of moles of gaseous substances involved in the reaction.
- This effectively lowers the total pressure in the reaction vessel.
- If the total number of moles of gaseous reactants equals to the total number of moles of gaseous products, the equilibrium is not affected by pressure or volume changes.
- AKA- Changes in V or P will cause equilibrium to shift if $\Delta n_{gas} \neq 0$.

2) Change in Volume



Shift in the direction with more gas molecules.

Shift in the direction with less gas molecules.

2) Change in Volume

$$A_{(g)} + B_{(g)} \rightleftharpoons C_{(g)}$$

Change	**Shifts the Equilibrium**	**Shift**
Increase volume	Side with most moles of gas	left
Decrease volume	Side with fewest moles of gas	right

Changes in V will not cause the equilibrium to shift if $\Delta n_{gas} = 0$.

$$A_{(g)} + B_{(g)} \rightleftharpoons C_{(g)} + B_{(g)}$$

or

$$A_{(g)} + B_{(g)} \rightleftharpoons 2C_{(g)}$$

3) Adding an Inert Gas

- Adding an inert gas has ***no effect*** on the equilibrium position, as long as the volume does not change.
  - Inert gas = a gas not involved in the reaction.
  - This is because all concentrations and partial pressures remain unchanged.

$$C_{(s)} + O_{2(g)} \rightleftharpoons CO_{2(g)}$$

Add N_2 to the reaction chamber.

$$K_p = \frac{P_{CO_2}}{P_{O_2}}$$

$$Q = \frac{P_{CO_2}}{P_{O_2}}$$

Q = K

Change in Pressure

$$A_{(g)} + B_{(g)} \rightleftharpoons C_{(g)}$$

We can change pressure in a reaction vessel three different ways:

1) Add A, B or C
   - -Changing the concentration of a gaseous component causes the equilibrium to shift according to LCP.
   - -Changing [Solids] and [liquids] do not influence the equilibrium.

2) Increasing or decreasing the volume of the chamber.
   - -Decreasing volume favors side with less gas molecules.
   - -Changes in volume do not affect s, l or aq species.

3) Adding an inert gas (a gas not involved in the rxn).
   - -Inert gas does not shift the reaction.

Changes in pressure have ***do not change*** the value of *K*.

Question:

How will **decreasing the volume** affect the equilibrium in each of the following reactions?

A) Shift Left B) Stay the same C) Shift right

1) $H_{2(g)} + I_{2(g)} \leftrightarrow 2HI_{(g)}$

2) $4NH_{3(g)} + 5O_{2(g)} \leftrightarrow 4NO_{(g)} + 6H_2O_{(g)}$

3) $CaF_{2(s)} \leftrightarrow Ca^{2+}_{(aq)} + 2F^{-}_{(aq)}$

4) $SO_{2(g)} + H_2O_{(l)} \leftrightarrow H_2SO_{3(aq)}$

5) $3Fe_{(s)} + 4H_2O_{(g)} \leftrightarrow Fe_3O_{4(s)} + 4H_{2(g)}$

Example Problem

How would you change the volume of each of the following reactions to *increase* the yield of the products?

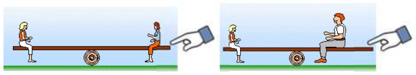
(a) $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$

(b) $S(s) + 3F_2(g) \rightleftharpoons SF_6(g)$

(c) $Cl_2(g) + I_2(g) \rightleftharpoons 2ICl(g)$

Factors that Affect Equilibrium

At equilibrium: $aA + bB \rightleftharpoons cC + dD$



How we will "poke" our equilibrium:

- Concentration ✓
- Pressure ✓
- Temperature
- Catalyst

Change in Temperature

Temperature changes both **the equilibrium concentrations and the equilibrium constant**.

$$A \rightleftharpoons B$$

$\text{rate}_{A\rightarrow B} = k_A\,[A]$

$\text{rate}_{B\rightarrow A} = k_B\,[B]$

$\text{rate}_{A\rightarrow B} = \text{rate}_{B\rightarrow A}$

$k_A\,[A] = k_B\,[B]$

Rate constant $_{A\rightarrow B}$

Rate constant $_{B\rightarrow A}$

$$\frac{k_A}{k_B} = \frac{[B]}{[A]} = \boxed{K}$$

Arrhenius Equation

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

k_A, k_B and K are temperature dependent!

Change in Temperature

To determine the effect of a change in temperature on equilibrium, heat is considered a component of the system.

Heat is a *product* in an *exothermic* reaction ($\Delta H^\circ_{rxn} < 0$ or $-\Delta H$).

$$aA + bB \rightleftharpoons cC + dD + \text{heat}$$

Heat is a *reactant* in an *endothermic* reaction ($\Delta H^\circ_{rxn} > 0$ or ΔH).

$$\textit{heat} + aA + bB \rightleftharpoons cC + dD$$

Change in Temperature

Heat is a *product* in an *exothermic* reaction ($\Delta H^\circ_{rxn} < 0$ or $-\Delta H$).

$$aA + bB \rightleftharpoons cC + dD + \text{heat}$$

What happens if we **increase** the temperature?

$$\overset{\xleftarrow{\hspace{3cm}}}{aA + bB \rightleftharpoons cC + dD} + \overset{\uparrow}{\text{heat}}$$

Heat is added

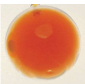
Reaction shifts left, K decreases

What happens if we **decrease** the temperature?

$$\overset{\xrightarrow{\hspace{3cm}}}{aA + bB \rightleftharpoons cC + dD} + \underset{\downarrow}{\text{heat}}$$

Heat is taken away

Reaction shifts right, K increases



Example

$N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$ $\Delta H° = 58.0$ kJ/mol

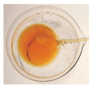
orange

$\text{Heat} + N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$

Which way does the reaction shift if:

we put it in an ice water bath?

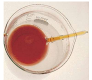
$\underset{\downarrow}{\text{Heat}} + \overleftarrow{N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}}$



K decreases

we put it in a hot water bath?

$\overset{\uparrow}{\text{Heat}} + \overrightarrow{N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}}$



K increases

Question:

Does an *increase* in temperature cause the following reactions to:

A) Shift Left B) Stay the same C) Shift right

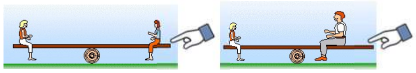
(1) $CaO_{(s)} + H_2O_{(g)} \rightleftharpoons Ca(OH)_{2(aq)}$ $\Delta H° = -82$ kJ

(2) $CaCO_{3(s)} \rightleftharpoons CaO_{(s)} + CO_{2(g)}$ $\Delta H° = 178$ kJ

(3) $SO_{2(g)} \rightleftharpoons S_{(s)} + O_{2(g)}$ $\Delta H° = 297$ kJ

Factors that Affect Equilibrium

At equilibrium: $aA + bB \rightleftharpoons cC + dD$

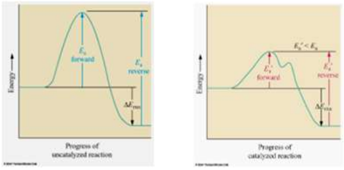


How we will “poke” our equilibrium:

- Concentration ✓
- Pressure ✓
- Temperature ✓
- Catalyst

Addition of a Catalyst

- A catalyst speeds up a reaction by lowering its activation energy.
- It speeds up the forward and reverse reactions equally.



- A catalyst causes a reaction to reach equilibrium more quickly.
- It does not change the equilibrium concentration or K.

Question:

How will the addition of a catalyst affect the equilibrium

A) Shift Left B) Stay the same C) Shift right

1) $2SO_{2(g)} + O_{2(g)} \leftrightarrow 2\ SO_{3(g)}$

2) $CO_{(g)} + H_2O_{(g)} \leftrightarrow CO_{2(g)} + H_{2(g)}$

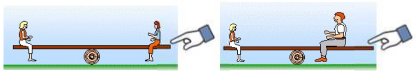
3) $CO_{(g)} + Cl_{2(g)} \leftrightarrow COCl_{2(g)}$

4) $N_2O_{4(g)} \leftrightarrow 2\ NO_{2(g)}$

5) $CO_{(g)} + 2H_{2(g)} \leftrightarrow CH_3OH_{(g)}$

Factors that Affect Equilibrium

At equilibrium: $aA + bB \rightleftharpoons cC + dD$



How we will "poke" our equilibrium:

- Concentration ✓
- Pressure ✓
- Temperature ✓
- Catalyst ✓

LCP Summary

Change	**Shift Equilibrium**	**Change Equilibrium Constant**
Concentration	yes	no
Volume	yes*	no
Temperature	yes	yes
Catalyst	no	no

*Dependent on relative moles of gaseous reactants and products

---

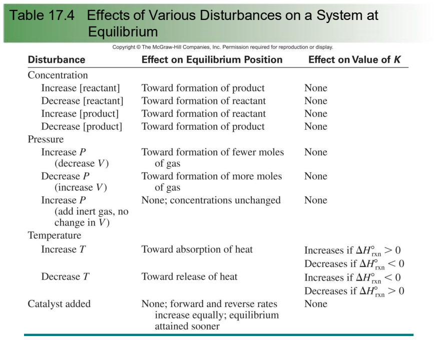


Table 17.4 Effects of Various Disturbances on a System at Equilibrium

Disturbance	**Effect on Equilibrium Position**	**Effect on Value of *K***
Concentration		
Increase [reactant]	Toward formation of product	None
Decrease [reactant]	Toward formation of reactant	None
Increase [product]	Toward formation of reactant	None
Decrease [product]	Toward formation of product	None
Pressure		
Increase P (decrease V)	Toward formation of fewer moles of gas	None
Decrease P (increase V)	Toward formation of more moles of gas	None
Increase P (add inert gas, no change in V)	None; concentrations unchanged	None
Temperature		
Increase T	Toward absorption of heat	Increases if $\Delta H^\circ_{rxn} > 0$ Decreases if $\Delta H^\circ_{rxn} < 0$
Decrease T	Toward release of heat	Increases if $\Delta H^\circ_{rxn} < 0$ Decreases if $\Delta H^\circ_{rxn} > 0$
Catalyst added	None; forward and reverse rates increase equally; equilibrium attained sooner	None

---

Consider the following equilibrium process between dinitrogen tetrafluoride (N_2F_4) and nitrogen difluoride (NF_2):

$$N_2F_4(g) \rightleftharpoons 2NF_2(g) \qquad \Delta H^\circ = 38.5 \text{ kJ/mol}$$

Predict the changes in the equilibrium and *K* if:

(a) the reacting mixture is heated at constant volume.

(b) some N_2F_4 gas is removed from the reacting mixture at constant temperature and volume.

(c) the pressure on the reacting mixture is decreased at constant temperature.

(d) a catalyst is added to the reacting mixture.

Consider the following equilibrium process between dinitrogen tetrafluoride (N_2F_4) and nitrogen difluoride (NF_2):

$N_2F_4(g) \rightleftharpoons 2NF_2(g)$ $\Delta H° = 38.5$ kJ/mol

Predict the changes in the equilibrium and K if:

(a) the reacting mixture is heated at constant volume.

$$\overset{\uparrow}{\text{Heat}} + \overset{\longrightarrow}{N_2F_{4(g)} \rightleftharpoons 2NF_{2(g)}}$$

Reaction shifts right, generates more product and increase K.

Consider the following equilibrium process between dinitrogen tetrafluoride (N_2F_4) and nitrogen difluoride (NF_2):

$N_2F_4(g) \rightleftharpoons 2NF_2(g)$ $\Delta H° = 38.5$ kJ/mol

Predict the changes in the equilibrium and K if:

(b) some N_2F_4 gas is removed from the reacting mixture at constant temperature and volume.

$$\text{Heat} + \underset{\downarrow}{N_2F_{4(g)}} \overset{\longleftarrow}{\rightleftharpoons} 2NF_{2(g)}$$

Reaction shifts left, generates more reactants and K stays the same.

Consider the following equilibrium process between dinitrogen tetrafluoride (N_2F_4) and nitrogen difluoride (NF_2):

$N_2F_4(g) \rightleftharpoons 2NF_2(g)$ $\Delta H° = 38.5$ kJ/mol

Predict the changes in the equilibrium and K if:

(c) the pressure on the reacting mixture is decreased at constant temperature.

pressure decrease = volume increase

$$\text{Heat} + \underset{\text{1 gas molecule}}{N_2F_{4(g)}} \overset{\longrightarrow}{\rightleftharpoons} \underset{\text{2 gas molecules}}{2NF_{2(g)}}$$

Reaction shifts right, generates more products and K stays the same.

Consider the following equilibrium process between dinitrogen tetrafluoride (N_2F_4) and nitrogen difluoride (NF_2):

$$N_2F_4(g) \rightleftharpoons 2NF_2(g) \qquad \Delta H° = 38.5 \text{ kJ/mol}$$

Predict the changes in the equilibrium and K if:
(d) a catalyst is added to the reacting mixture.

$$\text{Heat} + N_2F_{4(g)} \rightleftharpoons 2NF_{2(g)}$$

A catalyst causes a reaction to reach equilibrium more quickly.

It does not change the equilibrium concentration or K.

Real World Application

Haber-Bosch process:

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)} \qquad \Delta H°_{rxn} = -91.8 \text{ kJ}$$

You are tasked with feeding 7.3 billion people. NH_3 is crucial to increasing food production by maximizing crop yield.

How do you increase the rate of product formation?

Build more reactors.
Increase the temperature.
$\boxed{\text{Add a catalyst.}}$

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

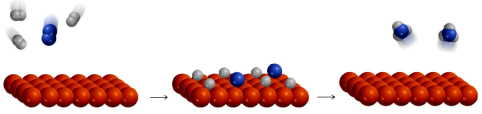
How do you shift the equilibrium to favor products?

Decrease the temperature.
Increase the pressure.
Decrease $[NH_3]$ by removing NH_3 as it forms.
Add more H_2 and N_2 as its consumed.

Important Heterogeneous Reactions

Haber-Bosch Reaction

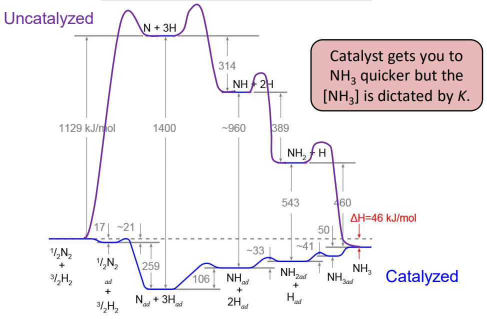
150 atm
400-600 °C



$$N_2\ (g) + 3H_2\ (g) \xrightarrow[\text{catalyst}]{Fe/Al_2O_3} 2NH_3\ (g)$$

Fritz Haber
1918 Nobel Prize in Chemistry

Haber-Bosch Process



Catalyst gets you to NH_3 quicker but the $[NH_3]$ is dictated by *K*.

Real World Application

Haber-Bosch process:

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)} \qquad \Delta H^\circ_{rxn} = -91.8\text{ kJ}$$

You are tasked with feeding 7.3 billion people. NH_3 is crucial to increasing food production by maximizing crop yield.

How do you increase the rate of product formation?

Build more reactors.
Increase the temperature.
Add a catalyst.

How do you shift the equilibrium to favor products?

Decrease the temperature.
Increase the pressure.
Decrease $[NH_3]$ by removing NH_3 as it forms.
Add more H_2 and N_2 as its consumed.

Haber-Bosch Process

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$$

$$\Delta H^\circ_{rxn} = -91.8\text{ kJ}$$

Which way does the reaction shift if:

we increase the temperature?

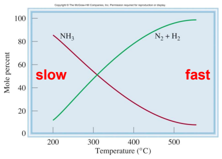
Reaction shifts left, less NH_3.
But…it gets there faster!

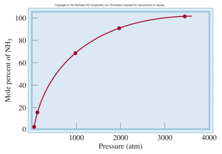
we decrease the temperature?

Reaction shifts right, more NH_3.
But…it gets there slower!

we increase the pressure?

Reaction shifts right, more NH_3.





Haber-Bosch Process

$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$

$\Delta H^\circ_{rxn} = -91.8$ kJ

Which way does the reaction shift if:

we increase the temperature?

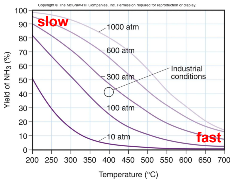
Reaction shifts left, less NH_3.
But…it gets there faster!

we decrease the temperature?

Reaction shifts right, more NH_3.
But…it gets there slower!

we increase the pressure?

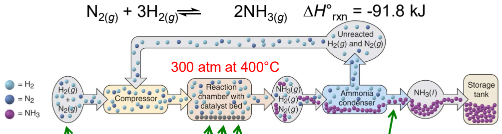
Reaction shifts right, more NH_3.



At very high *P* and low *T* (*top left*), the yield is high, but the reaction is slow. Industrial conditions (*circle*) are between 200 and 300 atm at about 400°C.

Haber-Bosch Process

$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$ $\Delta H^\circ_{rxn} = -91.8$ kJ



300 atm at 400°C

Increase the product formation rate:

Add a catalyst.
Increase the temperature.

Shift the equilibrium:

~~Decrease the temperature.~~
Increase the pressure.
Decrease $[NH_3]$ by removing NH_3 as it forms.
Add more H_2 and N_2 as its consumed.

Going one step further

If we are given the concentrations in a reaction mixture and K_c we can predict which direction the reaction will proceed.

$Q = K$: the system is at equilibrium
$Q < K$: the reaction proceeds to the right
$Q > K$: the reaction proceeds to the left

We can also calculate the concentrations of each species when it reaches equilibrium.

Reaction Table
ICE Table/Method

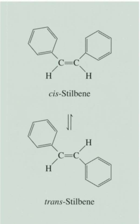
	cis-stilbene	⇌	*trans*-stilbene
Initial (*M*):	0.850		0
Change (*M*):	$-x$		$+x$
Equilibrium (*M*):	$(0.850 - x)$		x

ICE Method

cis-stilbene ⇌ *trans*-stilbene

The equilibrium constant (K_c) for this system is 24.0 at 200°C. Suppose that initially only *cis*-stilbene is present at a concentration of 0.850 mol/L. How do we calculate the concentrations of *cis*- and *trans*-stilbene at equilibrium?

- *Step 1*: Construct an ICE Table.
- *Step 2*: Insert known information into ICE Table (in M or pressure).
- *Step 3*: Determine the change in conc (x) that will occur as the reaction progresses.
- *Step 4*: Complete the table.
- *Step 5*: Set up K equation, calculate x.
- *Step 6*: Calculate equilibrium concs.



ICE Method

cis-stilbene ⇌ *trans*-stilbene

The equilibrium constant (K_c) for this system is 24.0 at 200°C. Suppose that initially only *cis*-stilbene is present at a concentration of 0.850 mol/L. How do we calculate the concentrations of *cis*- and *trans*-stilbene at equilibrium?

Step 1: Construct an ICE Table.

	Reactants		Products
	cis-stilbene	⇌	*trans*-stilbene
Initial (M):			
Change (M):			
Equilibrium (M):			

ICE Method

cis-stilbene ⇌ *trans*-stilbene

The equilibrium constant (K_c) for this system is 24.0 at 200°C. Suppose that initially only *cis*-stilbene is present at a concentration of 0.850 mol/L. How do we calculate the concentrations of *cis*- and *trans*-stilbene at equilibrium?

Step 2: Insert known information into ICE Table (in M or pressure).

	Reactants		Products
	cis-stilbene	⇌	*trans*-stilbene
Initial (M):	0.850		0
Change (M):			
Equilibrium (M):			

ICE Method

cis-stilbene $\rightleftharpoons$ *trans*-stilbene

The equilibrium constant (K_c) for this system is 24.0 at 200°C. Suppose that initially only *cis*-stilbene is present at a concentration of 0.850 mol/L. How do we calculate the concentrations of *cis*- and *trans*-stilbene at equilibrium?

Step 3: Determine the change in conc (x) that will occur.

	Reactants *cis*-stilbene	$\rightleftharpoons$	Products *trans*-stilbene
Initial (M):	0.850		0
Change (M):	-x		+x
Equilibrium (M):			

$$Q = \frac{[\text{trans}]}{[\text{cis}]} = 0$$

ICE Method

cis-stilbene $\rightleftharpoons$ *trans*-stilbene

The equilibrium constant (K_c) for this system is 24.0 at 200°C. Suppose that initially only *cis*-stilbene is present at a concentration of 0.850 mol/L. How do we calculate the concentrations of *cis*- and *trans*-stilbene at equilibrium?

Step 4: Complete the table.

	Reactants *cis*-stilbene	$\rightleftharpoons$	Products *trans*-stilbene
Initial (M):	0.850		0
Change (M):	-x		+x
Equilibrium (M):	(0.850 - x)		x

ICE Method

cis-stilbene $\rightleftharpoons$ *trans*-stilbene

The equilibrium constant (K_c) for this system is 24.0 at 200°C. Suppose that initially only *cis*-stilbene is present at a concentration of 0.850 mol/L. How do we calculate the concentrations of *cis*- and *trans*-stilbene at equilibrium?

Step 5: Set up K equation, calculate x.

	Reactants *cis*-stilbene	$\rightleftharpoons$	Products *trans*-stilbene
Initial (M):	0.850		0
Change (M):	-x		+x
Equilibrium (M):	(0.850 - x)		x

$$K = \frac{[\text{trans}]}{[\text{cis}]} = 24 = \frac{x}{0.850 - x} \qquad x = 0.816\text{ M}$$

ICE Method

cis-stilbene $\rightleftharpoons$ *trans*-stilbene

The equilibrium constant (K_c) for this system is 24.0 at 200°C. Suppose that initially only *cis*-stilbene is present at a concentration of 0.850 mol/L. How do we calculate the concentrations of *cis*- and *trans*-stilbene at equilibrium?

Step 5: Set up K equation, calculate x.

	Reactants		Products	
	cis-stilbene	$\rightleftharpoons$	*trans*-stilbene	
Initial (M):	0.850		0	
Change (M):	-x		+x	x = 0.816 M
Equilibrium (M):	(0.850 - x)		x	
Equilibrium:	0.034 M		0.816 M	

More Complex Example

The equilibrium constant K_c for the reaction $H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$ is 54.3 at 430°C. Suppose that the initial concentrations of H_2, I_2, and HI are 0.00623 *M*, 0.00414 *M*, and 0.0224 *M*, respectively. Calculate the concentrations of these species at equilibrium.

$$H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$$

$$\longrightarrow$$

$$K = \frac{[HI]^2}{[H_2]\,[I_2]} = \mathbf{54.3}$$

$$Q_c = \frac{[HI]_0^2}{[H_2]_0[I_2]_0} = \frac{(0.0224)^2}{(0.00623)(0.00414)} = 19.5$$

More Complex Example

The equilibrium constant K_c for the reaction $H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$ is 54.3 at 430°C. Suppose that the initial concentrations of H_2, I_2, and HI are 0.00623 *M*, 0.00414 *M*, and 0.0224 *M*, respectively. Calculate the concentrations of these species at equilibrium.

	Reactants				Products
	$H_{2(g)}$	+	$I_{2(g)}$	$\rightleftharpoons$	$2HI_{(g)}$
Initial (M):	0.00623		0.00414		0.0224
Change (M):	- x		- x		2x
Equilibrium (M):	(0.00623 – x)		(0.00414 – x)		0.0224 + 2x

$$K_c = \frac{[HI]^2}{[H_2][I_2]} \qquad 54.3 = \frac{(0.0224 + 2x)^2}{(0.00623 - x)(0.00414 - x)}$$

More Complex Example

Then math happens!

$$K_c = \frac{[HI]^2}{[H_2][I_2]} = 54.3 = \frac{(0.0224 + 2x)^2}{(0.00623 - x)(0.00414 - x)}$$

$$54.3(2.58 \times 10^{-5} - 0.0104x + x^2) = 5.02 \times 10^{-4} + 0.0896x + 4x^2$$

$$50.3x^2 - 0.654x + 8.98 \times 10^{-4} = 0$$

This is a quadratic equation of the form $ax^2 + bx + c = 0$.
(a = 50.3, b = -0.654, and c = 8.98×10^{-4})

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

$$x = \frac{0.654 \pm \sqrt{(-0.654)^2 - 4(50.3)(8.98 \times 10^{-4})}}{2 \times 50.3}$$

$x = 0.0114\ M$ or $x = 0.00156\ M$

More Complex Example

The equilibrium constant K_c for the reaction $H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$ is 54.3 at 430°C. Suppose that the initial concentrations of H_2, I_2, and HI are 0.00623 M, 0.00414 M, and 0.0224 M, respectively. Calculate the concentrations of these species at equilibrium.

	Reactants				Products
	$H_{2(g)}$	+	$I_{2(g)}$	$\rightleftharpoons$	$2HI_{(g)}$
Initial (M):	0.00623		0.00414		0.0224
Change (M):	- x		- x		2x
Equilibrium (M):	(0.00623 – x)		(0.00414 – x)		0.0224 + 2x

Equilibrium:

$$x = \frac{0.654 \pm \sqrt{(-0.654)^2 - 4(50.3)(8.98 \times 10^{-4})}}{2 \times 50.3}$$

$x = 0.0114\ M$ or $x = 0.00156\ M$

Question : A B

More Complex Example

The equilibrium constant K_c for the reaction $H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$ is 54.3 at 430°C. Suppose that the initial concentrations of H_2, I_2, and HI are 0.00623 M, 0.00414 M, and 0.0224 M, respectively. Calculate the concentrations of these species at equilibrium.

	Reactants				Products
	$H_{2(g)}$	+	$I_{2(g)}$	$\rightleftharpoons$	$2HI_{(g)}$
Initial (M):	0.00623		0.00414		0.0224
Change (M):	- x		- x		2x
Equilibrium (M):	(0.00623 – x)		(0.00414 – x)		0.0224 + 2x
Equilibrium:	0.00467 M		0.00258 M		0.0255 M

$x = 0.00156\ M$

There has to be a better way!

Sometimes close enough is good enough!

We can assume that $[A]_{init} - x \approx [A]_{init}$ if:

- K_c is relatively small

  and/or

- $[A]_{init}$ is relatively large.

if $\frac{\text{approximate } x}{\text{initial concentration}} \times 100\%$ <5% the approximation is vaild

If $\frac{[A]_{init}}{K_c} > 400$, the assumption is justified; neglecting x introduces an error < 5%.

If $\frac{[A]_{init}}{K_c} < 400$, the assumption is not justified; neglecting x introduces an error > 5%.

Another Example

A reaction chamber contains 0.8 M of N_2, 0.2 M of oxygen, and 0 M of NO at 1500 K. Is the mixture at equilibrium. If not, which way will it shift and by how much?

$$\underrightarrow{N_2 + O_2 \rightleftharpoons 2\,NO} \quad K_c = 1.0 \times 10^{-5} \text{ at } 1500\text{ K}$$

$$Q = \frac{[NO]^2}{[N_2]\,[O_2]} = \frac{(0)^2}{(0.8)\ (0.2)} = 0$$

Another Example

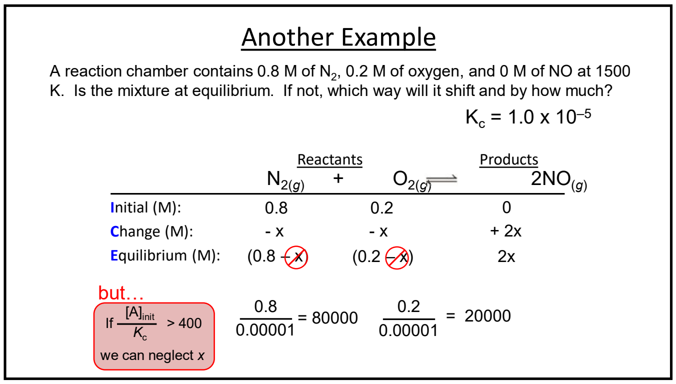
A reaction chamber contains 0.8 M of N_2, 0.2 M of oxygen, and 0 M of NO at 1500 K. Is the mixture at equilibrium. If not, which way will it shift and by how much?

$K_c = 1.0 \times 10^{-5}$

	Reactants				Products
	$N_{2(g)}$	+	$O_{2(g)}$	$\rightleftharpoons$	$2NO_{(g)}$
Initial (M):	0.8		0.2		0
Change (M):	- x		- x		+ 2x
Equilibrium (M):	(0.8 – x)		(0.2 – x)		2x

$$K = \frac{[NO]^2}{[N_2]\,[O_2]} = \frac{(2x)^2}{(0.8 - x)(0.2 - x)}$$

$4x^2 + 0.00399x + 1.6 \times 10^{-6} = 0$ etc.



Another Example

A reaction chamber contains 0.8 M of N_2, 0.2 M of oxygen, and 0 M of NO at 1500 K. Is the mixture at equilibrium. If not, which way will it shift and by how much?

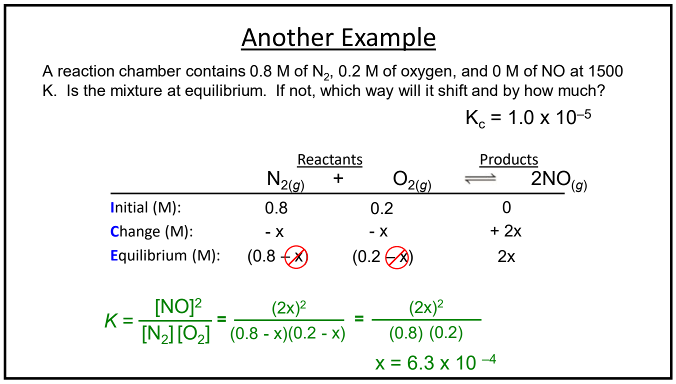
$K_c = 1.0 \times 10^{-5}$

	Reactants				Products
	$N_{2(g)}$	+	$O_{2(g)}$	⇌	$2NO_{(g)}$
Initial (M):	0.8		0.2		0
Change (M):	- x		- x		+ 2x
Equilibrium (M):	$(0.8 \cancel{- x})$		$(0.2 \cancel{- x})$		2x

but…

If $\frac{[A]_{init}}{K_c} > 400$ we can neglect *x*

$\frac{0.8}{0.00001} = 80000$ $\frac{0.2}{0.00001} = 20000$



Another Example

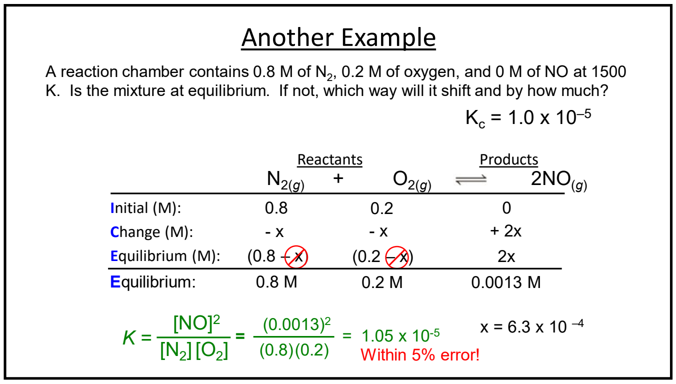
A reaction chamber contains 0.8 M of N_2, 0.2 M of oxygen, and 0 M of NO at 1500 K. Is the mixture at equilibrium. If not, which way will it shift and by how much?

$K_c = 1.0 \times 10^{-5}$

	Reactants				Products
	$N_{2(g)}$	+	$O_{2(g)}$	⇌	$2NO_{(g)}$
Initial (M):	0.8		0.2		0
Change (M):	- x		- x		+ 2x
Equilibrium (M):	$(0.8 \cancel{- x})$		$(0.2 \cancel{- x})$		2x

$$K = \frac{[NO]^2}{[N_2][O_2]} = \frac{(2x)^2}{(0.8 - x)(0.2 - x)} = \frac{(2x)^2}{(0.8)\ (0.2)}$$

$x = 6.3 \times 10^{-4}$



Another Example

A reaction chamber contains 0.8 M of N_2, 0.2 M of oxygen, and 0 M of NO at 1500 K. Is the mixture at equilibrium. If not, which way will it shift and by how much?

$K_c = 1.0 \times 10^{-5}$

	Reactants				Products
	$N_{2(g)}$	+	$O_{2(g)}$	⇌	$2NO_{(g)}$
Initial (M):	0.8		0.2		0
Change (M):	- x		- x		+ 2x
Equilibrium (M):	$(0.8 \cancel{- x})$		$(0.2 \cancel{- x})$		2x
Equilibrium:	0.8 M		0.2 M		0.0013 M

$$K = \frac{[NO]^2}{[N_2][O_2]} = \frac{(0.0013)^2}{(0.8)(0.2)} = 1.05 \times 10^{-5}$$

$x = 6.3 \times 10^{-4}$

Within 5% error!

ICE Method

PRELIMINARY SETTING UP

1. Write the balanced equation.
2. Write the reaction quotient, *Q*.
3. Convert all amounts into the correct units (*M* or atm).

WORKING ON THE REACTION TABLE

4. When reaction direction is not known, compare *Q* with *K*.
5. Construct a reaction table.

✓ Check the sign of x, the change in the concentration (or pressure).

ICE Method

SOLVING FOR x AND EQUILIBRIUM QUANTITIES

6. Substitute the quantities into *K* equation.
7. To simplify the math, assume that x is negligible:

$$([A]_{init} - x = [A]_{eq} \approx [A]_{init})$$

8. Solve for x.

✓ Check that assumption is justified (<5% error). If not, solve quadratic equation for x.

9. Find the equilibrium quantities.

✓ Check to see that calculated values give the known *K*.

$$\text{if } \frac{\text{approximate } x}{\text{initial concentration}} \times 100\% < 5\% \text{ the approximation is vaild}$$

Question?