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 **MCAT General Chemistry**
Kinetics & Equilibrium

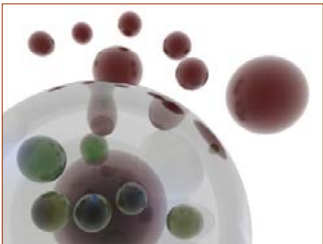
Rapid Learning MCAT Series

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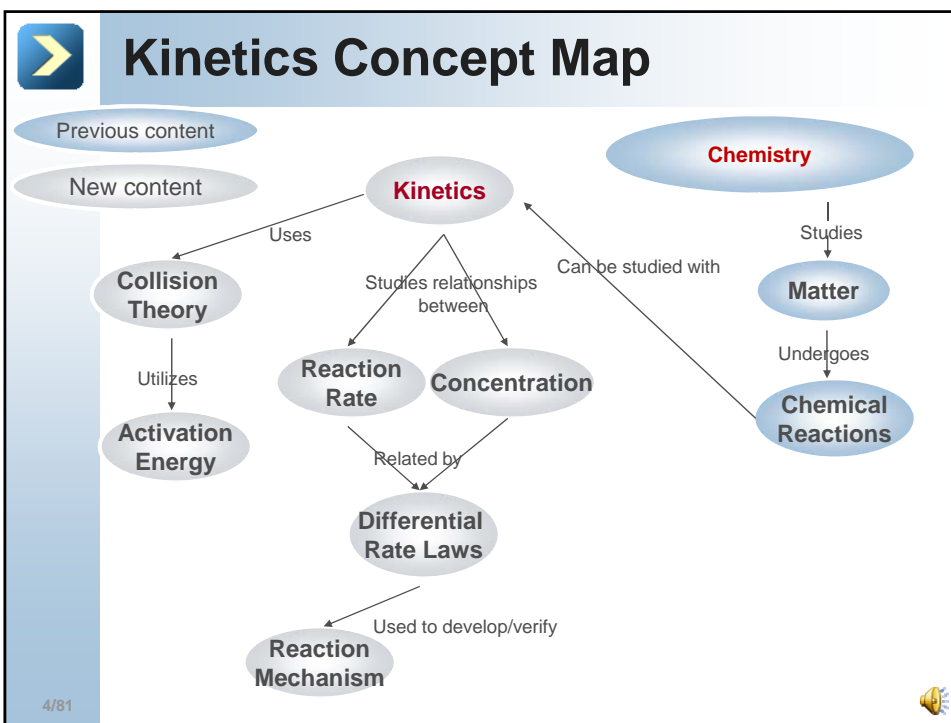
Learning Objectives

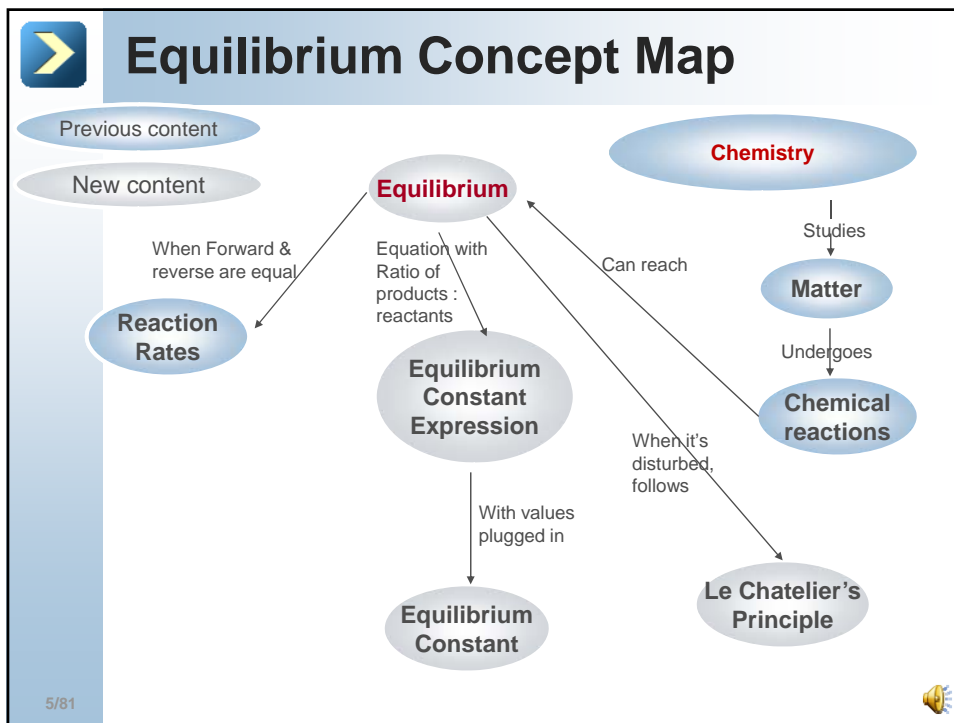
By completing this tutorial you will learn...




- What Kinetics studies
- Collision Theory
- Reaction coordinate diagrams
- Which factors affect rate
- Reaction mechanisms
- Rate laws
- Dynamic equilibrium
- Equilibrium constants
- Le Chatelier's Principle
- Free Energy & Equilibrium


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Kinetics and Reaction Coordinate Diagrams



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Definitions - Kinetics & Reaction Rates

Kinetics – The study of the rates of reactions.

Reaction Rate – Rate at which reactants produce products.
How fast a reaction takes place.



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Definition - Collision Theory

Collision Theory – Defines 3 circumstances to be met for a collision to occur.

- 1 Reactants must collide.
- 2 Collision must be at the correct orientation.
- 3 Collision must have sufficient energy for reaction to occur.



Only a small fraction of collisions meet the requirements and results in a successful reaction.

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Collisions Must Occur

In order for two molecules to react, they must come into contact with one another.



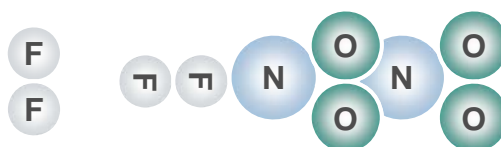
There is no way they will ever react if they don't run into one another!

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Collision with Correct Orientation

For a collision to result in a chemical reaction, it must occur with the correct orientation.



This is not the correct orientation. The reaction will not happen.

This is the correct orientation. The reaction will happen.

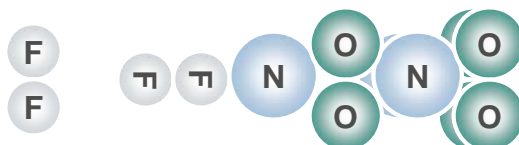
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Collision with Enough Energy

For a collision to result in a chemical reaction, it must occur with the minimum energy for reaction.



The collision does not have enough energy to produce a reaction.

This collision had more energy (faster moving molecules). A reaction will occur..

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Definition - Activation Energy

Activation Energy
– Energy that must be overcome for reaction to occur.



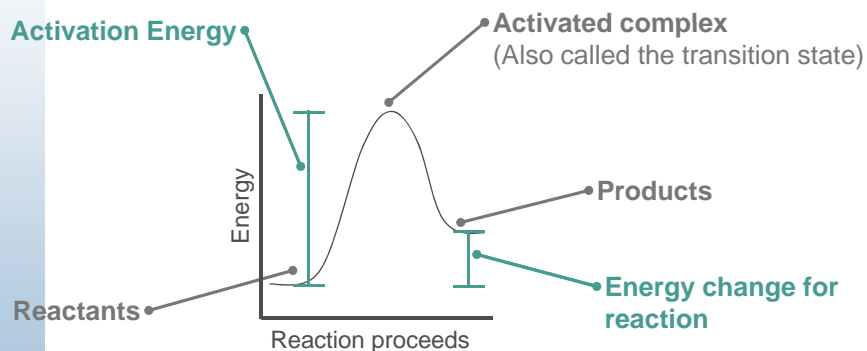
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Reaction Coordinate Diagram

Reaction coordinate diagrams show the energy changes throughout the reaction.

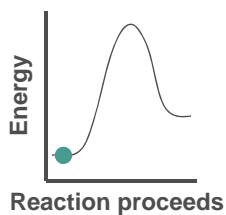


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Activated Complex

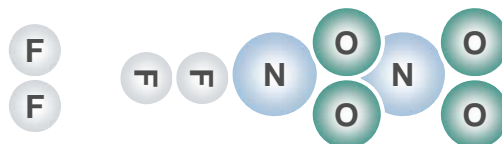
What is an “activated complex” or “transition state”?



Reactants $F_2 + NO_2$

Activated Complex $F_2 \cdots NO_2$

Products $F + FNO_2$



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Definition - Endo & Exothermic

Endothermic Reaction – The reaction takes in energy...the products have more energy than the reactants.

Exothermic Reaction – The reaction gives off energy...the products have less energy than the reactants.

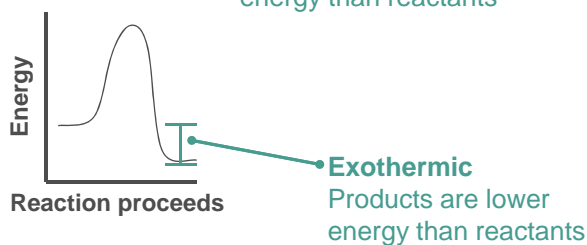
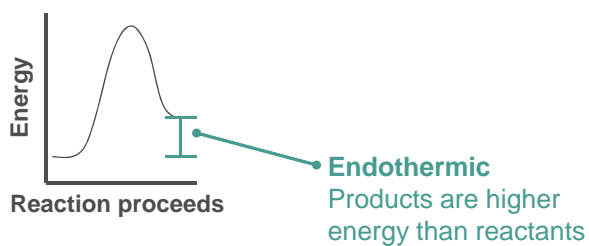


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Endo- and Exothermic Diagrams

Reaction coordinate diagrams show whether a reaction is endothermic or exothermic.



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Factors Affecting Reaction Rates



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Surface Area of Reactants

How does the surface area of the reactants affect the reaction rate?

Reactants must collide in order to react.


➔

Larger surface area means more particles can come in contact with each other at the same time.

➔

More reactants can collide at the same time and a fraction of those will result in reaction.

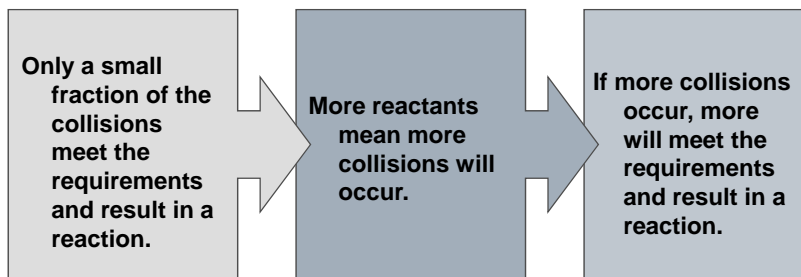
As surface area increases, reaction rate increases.

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Concentrations of Reactants

How does the concentration of reactants affect the reaction rate?



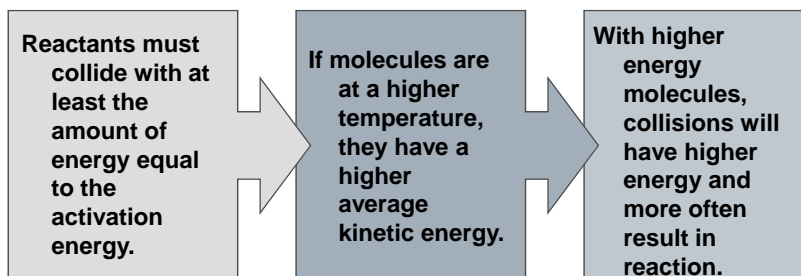
As reactant concentration increases, reaction rate increases.

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Temperature

How does temperature affect the reaction rate?



For most reactions, as temperature increases, reaction rate increases.

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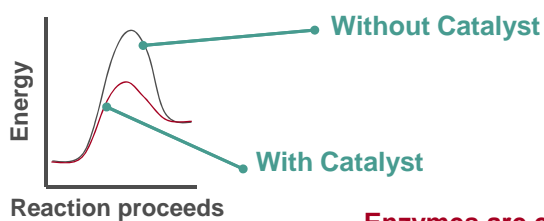


Definition--Catalysts

Catalysts – Substance that increases the rate of reaction without being used up.



“C” is the catalyst...it is present in the beginning and at the end.



Enzymes are catalysts in the body.

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Catalysts

How do catalysts help speed up the reaction without being used?

They increase the chances that a collision will successfully produce a reaction.


For example, catalysts hold one or more of the reactants in place to allow collisions to occur with the correct orientation.

Once the reaction has occurred, the catalyst releases the molecule(s) and finds another one to help.




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Reaction Mechanisms




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Definition - Reaction Mechanisms

Elementary Step – Chemical equation that shows which molecules collide with other molecules.

Reaction Mechanism – Set of elementary steps that add up to the overall reaction.



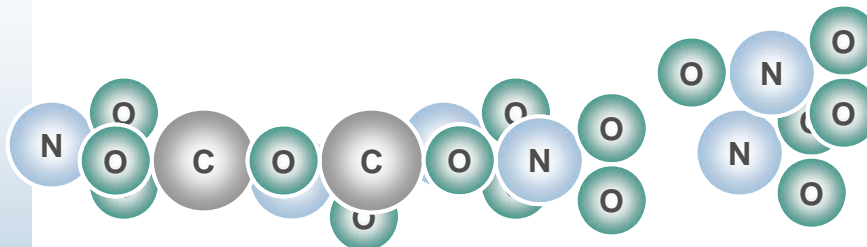
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Elementary Steps

Elementary steps show which molecules actually collide.

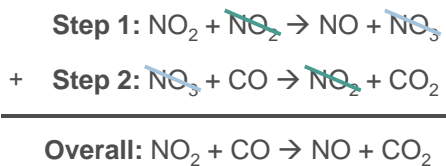


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Reaction Mechanism

The elementary steps must add up to equal the overall chemical reaction.



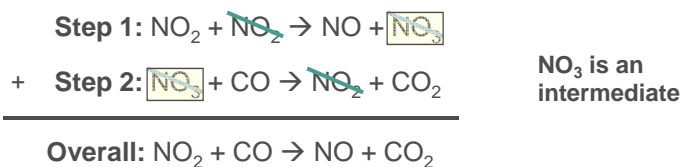
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Definition - Intermediate

Intermediate – Species that is in the mechanism, but does not appear in the overall equation (it appears and disappears).



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Definition—Rate Determining Step

Rate Determining Step – The slowest elementary step in the mechanism.

The bottleneck...it slows things down and determines the rate.

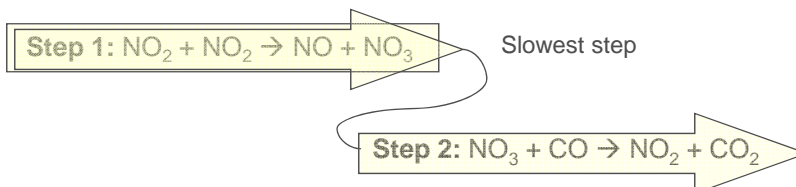
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Rate Determining Step

How does the rate determining step dictate the rate of reaction?



As quickly as the first reaction happens, the second reaction occurs.

The overall reaction is “waiting” for the first step to be completely, and then the overall can be completed.

The rate of the overall reaction is affected the greatest by the rate of the first step.

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Rate Laws



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Definition - Rate Law

Rate Law – The mathematical equation describing the rate of the equation.

Rate Laws cannot be determined from the overall chemical equation.

Rate Laws are determined by experiment only.



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Rate Laws and Reaction Mechanism

How do rate laws and reaction mechanisms relate?

A proposed mechanism can be determined, verified or discounted if it does not match the experimentally determined rate law.

Rate laws match the rate determining elementary step of a mechanism.



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Definition - Differential Rate Law

Differential Rate Law – How rate depends on concentration of reactants.



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Differential Rate Law

Differential Rate Laws have the following format:

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

Rate = rate of reaction (in units of M/s)

k = rate law constant. Different for every reaction at each temperature.

[A] & **[B]** = concentrations (in Molarity, M) of reactants that must collide in the rate determining step.

n and **m** = molecularity (or “order”) of reactants (how many of each reactant must collide).

How many are colliding together.

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Definition - Rate Order

Rate Order – The number of that molecule that must collide in the rate determining step.



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Rate Order, Concentration and Rate

How does the rate order affect how a change in concentration changes the rate?

Order	Symbol	Doubling concentration of "A" will ___ the rate
0	$[A]^0$ (or $[A]$ not mentioned at all)	Have no affect on $[x2]^0 = x1$
1	$[A]^1$ or $[A]$	Double $[x2]^1 = x2$
2	$[A]^2$	Quadruple $[x2]^2 = x4$

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Determining Differential Rate Law - 1

How do you determine the differential rate law from experimental data?

- Choose two trials (where only one concentration is changed). Set the ratio of their rates = the ratio of their rate laws

Trial	$[\text{NH}_4^+]$	$[\text{NO}_2^-]$	Rate
1	0.100 M	0.0050 M	1.35×10^{-7} M/s
2	0.100 M	0.010 M	2.70×10^{-7} M/s
3	0.200 M	0.010 M	5.40×10^{-7} M/s

$$\frac{\text{Rate}_1}{\text{Rate}_2} = \frac{k[\text{NH}_4^+]_1^n [\text{NO}_2^-]_1^m}{k[\text{NH}_4^+]_2^n [\text{NO}_2^-]_2^m} \quad \longrightarrow \quad \frac{1.35 \times 10^{-7}}{2.70 \times 10^{-7}} = \frac{k[0.100\text{M}]^n [0.0050]^m}{k[0.100\text{M}]^n [0.010]^m}$$

$$\frac{1}{2} = \frac{[0.0050]^m}{[0.010]^m} \quad \longrightarrow \quad \frac{1}{2} = \left(\frac{0.0050}{0.010}\right)^m \quad \longrightarrow \quad \frac{1}{2} = \left(\frac{1}{2}\right)^m \quad m = 1$$

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Determining Differential Rate Law - 2

How do you determine the differential rate law from experimental data?

- Repeat for other sets of trials until all orders are determined (the last one doesn't need all other reactants held constant—you'll already know their orders)

Trial	$[\text{NH}_4^+]$	$[\text{NO}_2^-]$	Rate
1	0.100 M	0.0050 M	1.35×10^{-7} M/s
2	0.100 M	0.010 M	2.70×10^{-7} M/s
3	0.200 M	0.010 M	5.40×10^{-7} M/s

$$\frac{\text{Rate}_2}{\text{Rate}_3} = \frac{k[\text{NH}_4^+]_2^n [\text{NO}_2^-]_2^m}{k[\text{NH}_4^+]_3^n [\text{NO}_2^-]_3^m} \quad \longrightarrow \quad \frac{2.70 \times 10^{-7}}{5.40 \times 10^{-7}} = \frac{k[0.100\text{M}]^n [0.010]^m}{k[0.200\text{M}]^n [0.010]^m}$$

$$\frac{1}{2} = \frac{[0.100]^n}{[0.200]^n} \quad \longrightarrow \quad \frac{1}{2} = \left(\frac{0.100}{0.200}\right)^n \quad \longrightarrow \quad \frac{1}{2} = \left(\frac{1}{2}\right)^n \quad n = 1$$

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Determining Differential Rate Law - 3

How do you determine the differential rate law from experimental data?

- 3 Use one trial's data and the determined orders to solve for k

Trial	[NH ₄ ⁺]	[NO ₂ ⁻]	Rate
1	0.100 M	0.0050 M	1.35 × 10 ⁻⁷ M/s
2	0.100 M	0.010 M	2.70 × 10 ⁻⁷ M/s
3	0.200 M	0.010 M	5.40 × 10 ⁻⁷ M/s

$$\text{Rate} = k[\text{NH}_4^+]^1[\text{NO}_2^-]^1$$

$$1.35 \times 10^{-7} \text{ M/s} = k(0.100 \text{ M})^1(0.0050 \text{ M})^1$$

$$\frac{1.35 \times 10^{-7} \text{ M/s}}{(0.100 \text{ M})(0.0050 \text{ M})} = k$$

$$k = 2.7 \times 10^{-4} (\text{M} \times \text{s})^{-1}$$

$$\text{Rate} = (2.7 \times 10^{-4} \text{ 1/M} \times \text{s}) [\text{NH}_4^+]^1 [\text{NO}_2^-]^1$$

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A Short-Cut Method - 1

By examining the affect of changing each reactant, the orders can be determined.

This method only works if you can find a pair of trials for each reactant that only vary that reactant.

Trial	[BrO ₃ ⁻¹]	[Br ⁻¹]	[H ⁺]	Rate
1	0.10 M	0.10 M	0.10 M	8.0 × 10 ⁻⁴ M/s
2	0.20 M	0.10 M	0.10 M	1.6 × 10 ⁻³ M/s
3	0.20 M	0.20 M	0.10 M	3.2 × 10 ⁻³ M/s
4	0.10 M	0.10 M	0.20 M	3.2 × 10 ⁻³ M/s

Trials 1 & 2—all are held constant except BrO₃⁻¹

It's doubled from trial 1 to trail 2

The rate also doubles.

BrO₃⁻¹ is first order

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A Short-Cut Method - 2

By examining the affect of changing each reactant, the orders can be determined.

This method only works if you can find a pair of trials for each reactant that only vary that reactant.

Trial	[BrO ₃ ⁻¹]	[Br ⁻¹]	[H ⁺]	Rate
1	0.10 M	0.10 M	0.10 M	8.0 × 10 ⁻⁴ M/s
2	0.20 M	0.10 M	0.10 M	1.6 × 10 ⁻³ M/s
3	0.20 M	0.20 M	0.10 M	3.2 × 10 ⁻³ M/s
4	0.10 M	0.10 M	0.20 M	3.2 × 10 ⁻³ M/s

Trials 2 & 3—all are held constant except Br⁻¹
It's doubled from trial 2 to trail 3
The rate also doubles.
Br⁻¹ is first order

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A Short-Cut Method - 3

By examining the affect of changing each reactant, the orders can be determined.

This method only works if you can find a pair of trials for each reactant that only vary that reactant.

Trial	[BrO ₃ ⁻¹]	[Br ⁻¹]	[H ⁺]	Rate
1	0.10 M	0.10 M	0.10 M	8.0 × 10 ⁻⁴ M/s
2	0.20 M	0.10 M	0.10 M	1.6 × 10 ⁻³ M/s
3	0.20 M	0.20 M	0.10 M	3.2 × 10 ⁻³ M/s
4	0.10 M	0.10 M	0.20 M	3.2 × 10 ⁻³ M/s

Trials 1 & 4—all are held constant except H⁺
It's doubled from trial 1 to trail 4
The rate is increased x4.
H⁺ is second order

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A Short-Cut Method - 4

By examining the affect of changing each reactant, the orders can be determined.

This method only works if you can find a pair of trials for each reactant that only vary that reactant.

Trial	[BrO ₃ ⁻¹]	[Br ⁻¹]	[H ⁺]	Rate
1	0.10 M	0.10 M	0.10 M	8.0 × 10 ⁻⁴ M/s
2	0.20 M	0.10 M	0.10 M	1.6 × 10 ⁻³ M/s
3	0.20 M	0.20 M	0.10 M	3.2 × 10 ⁻³ M/s
4	0.10 M	0.10 M	0.20 M	3.2 × 10 ⁻³ M/s

$$\text{Rate} = k[\text{BrO}_3^{-1}]^1[\text{Br}^{-1}]^1[\text{H}^{+1}]^2$$

$$8.0 \times 10^{-4} \text{ M/s} = k(0.10\text{M})(0.10\text{M})(0.10\text{M})^2$$

$$k = 8.0 (\text{M}^3 \times \text{s})^{-1}$$

$$\frac{8.0 \times 10^{-4} \text{ M/s}}{(0.10\text{M})(0.10\text{M})(0.10\text{M})^2} = k$$

$$\text{Rate} = \left(8.0 \frac{1}{\text{M}^3 \text{s}}\right) [\text{BrO}_3^{-1}]^1 [\text{Br}^{-1}]^1 [\text{H}^{+1}]^2$$

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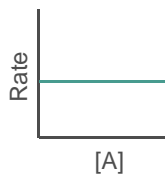


Graphical Determination of Order

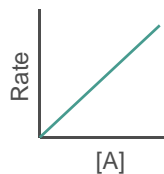
Graphing experimental data can also give the rate order.

If X-axis	And Y-axis	Give	Then...order
[A]	Rate	Flat line (zero slope)	0
[A]	Rate	Straight line	1
[A]	√ Rate	Straight line	2

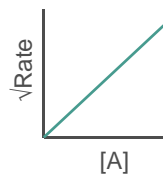
0 Order



1 Order



2 Order



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Reaction Rates and Temperature



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Definition - Activation Energy

Activation Energy (E_A) – Minimum energy of a collision resulting in a reaction.



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➤ Rate, Activation Energy & Temperature

How does the activation energy affect the rate?

```


    graph LR
      A[Higher activation energy] --> B[Lower likelihood of collisions resulting in a reaction]
      B --> C[Slower rate...it takes longer to get a collision to produce a reaction]
    
```



What role does temperature play?


```

    graph LR
      D[High temperature = molecules with higher energy] --> E[Collisions will happen with more energy, more likely to be above activation energy]
      E --> F[Rate increases]
    
```

As temperature increases, rate increases.

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 **Equilibrium** 

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Definition - Equilibrium

Reversible Reaction – A chemical reaction that can proceed in both directions (represented by a “ \rightleftharpoons ”).

Equilibrium – When the rate of the forward reaction equals the rate of the reverse reaction.

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Establishing Equilibrium

It takes time to establish equilibrium.



At first, there are only reactants present. Only the forward reaction is possible.

- But once there are products as well, they can begin to reform reactants.
- The reverse reaction becomes possible. Forward rate slows and reverse rate increases until they are the same.
- Once the rate of the forward and reverse process are equal, the reaction is in equilibrium.
- When equilibrium is established, the number of products and reactants doesn't change...but the reaction keeps going.

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Definition - Dynamic Equilibrium

Dynamic Equilibrium – The reaction continues to proceed in both directions, but at the same rate.

The number of products and reactants no longer change, it may appear as if the reaction has stopped...

But the reaction continues!



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Equilibrium Constants



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Definition - Equilibrium Constant

Equilibrium Constant Expression – Equation showing the ratio of the concentrations of products to reactants at equilibrium.

Concentration is symbolized with brackets “[A]”.

Equilibrium Constant (K) – The number calculated from the equilibrium constant expression.

“K” is different for every reaction at every temperature!

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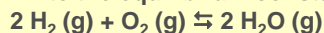


Writing Equilibrium Constant Expressions

To write an equilibrium constant expression:

- 1 Write the concentration of products on the top—take each one to a power of the coefficient in the balanced equation.
- 2 Write the concentration of reactants on the bottom—also take each to the power of the balanced equation coefficient.

Example: Write the equilibrium constant expression for the following:



$$K = \frac{[\text{H}_2\text{O}]^2}{[\text{H}_2]^2[\text{O}_2]}$$

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Definition: Homo- and Heterogeneous Equilibrium

Homogeneous Equilibrium – All of the species are the same state of matter.



Heterogeneous Equilibrium – There are at least 2 states of matter.



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Concentrations of Solids and Liquids

Pure solids and pure liquids have constant “concentrations”.

If concentration (Molarity) = $\frac{\text{mole}}{\text{liters}}$

And Density = $\frac{\text{grams}}{\text{liters}}$

And Molar Mass = $\frac{\text{grams}}{\text{mole}}$

Then for a pure solid or liquid, Molarity = $\frac{\text{grams / liters}}{\text{grams / mole}}$

Or, Molarity = $\frac{\text{Density}}{\text{Molar Mass}}$



Both Density and Molar Mass are constants—they don't change. Therefore, “concentration” of a pure solid or liquid is a constant.

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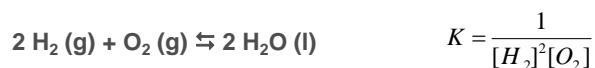




“K” Expressions with Solids or Liquids

How does this affect the writing of Equilibrium Constant Expressions?

If the “concentration” of a pure solid or liquid is constant, then it will not change during equilibrium and it is not written in the “K” expression.



H₂O is not included in this “K” expression because it’s a liquid.

Only gases and solutions are included in “K” expressions!

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Calculating “K” Example

Example: Solve for equilibrium constant for $\text{Fe}_2\text{O}_3 (\text{s}) + 3 \text{H}_2 (\text{g}) \rightleftharpoons 2 \text{Fe} (\text{s}) + 3 \text{H}_2\text{O} (\text{g})$ if the following are concentrations at equilibrium: $[\text{H}_2] = 0.45 \text{ M}$ and $[\text{H}_2\text{O}] = 0.18 \text{ M}$

$$[\text{H}_2]_{\text{eq}} = 0.45 \text{ M}$$

$$[\text{H}_2\text{O}]_{\text{eq}} = 0.18 \text{ M}$$

$$K = ?$$

$$K = \frac{[\text{H}_2\text{O}]^3}{[\text{H}_2]^3}$$

Note that Fe₂O₃ and Fe were not included in the K expression as they are solids!

$$K = \frac{[0.18]^3}{[0.45]^3}$$

$$K = 0.064$$

Most instructors and textbooks do not require units for “K” because each would be different.

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Meaning of Equilibrium Constant

What general meaning can you get from the magnitude of the equilibrium constant?

If K is very large...
$$\frac{[\text{Products}]}{[\text{Reactants}]}$$

There is a much larger ratio of products to reactants at equilibrium.

The reaction is said to “**lie to the right**” (products are on the right).

If K is very small...
$$\frac{[\text{Products}]}{[\text{Reactants}]}$$

There is a much smaller ratio of products to reactants at equilibrium.

The reaction is said to “**lie to the left**”.

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Using “K” to Find Equilibrium Concentration

Example: Find the equilibrium concentration for NO if the equilibrium constant for $\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2 \text{NO}(\text{g})$ is 1.24×10^{-4} , and the other equilibrium concentrations are $[\text{N}_2] = 0.166 \text{ M}$ and $[\text{O}_2] = 0.145 \text{ M}$

$$[\text{N}_2]_{\text{eq}} = 0.166 \text{ M}$$

$$[\text{O}_2]_{\text{eq}} = 0.145 \text{ M}$$

$$K = 1.24 \times 10^{-4}$$

$$[\text{NO}]_{\text{eq}} = ? \text{ M}$$

$$K = \frac{[\text{NO}]^2}{[\text{N}_2][\text{O}_2]}$$

$$1.24 \times 10^{-4} = \frac{[\text{NO}]^2}{(0.166 \text{ M})(0.145 \text{ M})}$$

$$\sqrt{(1.24 \times 10^{-4})(0.166 \text{ M})(0.145 \text{ M})} = [\text{NO}]$$

$$[\text{NO}]_{\text{eq}} = 0.00173 \text{ M}$$

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Le Chatelier's Principle




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Definition - Le Chatelier's Principle

Le Chatelier's Principle –
If a system at equilibrium
is disturbed, it will shift
to re-establish
equilibrium.

A system will try to undo
whatever you've done.



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➤ Increasing Concentrations

How does adding a reactant or product affect a system at equilibrium?

Adding a reactant

➔

Q becomes too small

➔

Reaction shifts to right
 (get rid of extra reactants and make more products)

Adding a product

➔

Q becomes too large

➔

Reaction shifts to left
 (get rid of extra products and make more reactants)

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➤ Decreasing Concentrations

How does removing a reactant or product affect a system at equilibrium?

Removing a reactant

➔

Q becomes too large

➔

Reaction shifts to left
 (make more reactants)

Removing a product

➔

Q becomes too small

➔

Reaction shifts to right
 (make more products)

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Changes in Pressure

How does changing the pressure affect a system at equilibrium?

The diagram consists of two rows of boxes connected by arrows. The top row shows a light gray box labeled 'Decrease volume' with an arrow pointing to a darker gray box labeled 'Pressure increases', which then has an arrow pointing to a light gray box labeled 'Reaction shifts to the side with least moles of gas to decrease pressure'. The bottom row shows a light gray box labeled 'Increase volume' with an arrow pointing to a darker gray box labeled 'Pressure decreases', which then has an arrow pointing to a light gray box labeled 'Reactions shifts to the side with the most moles of gas to increase pressure'. A small speaker icon is in the bottom right corner of the slide.

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Definition - Endo & Exothermic Reactions

Endothermic Reaction – The reaction takes in energy...the products have more energy than the reactants.

Energy is a reactant in the reaction.

Exothermic Reaction – The reaction gives off energy...the products have less energy than the reactants.

Energy is a product in the reaction.

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Temperature and Endothermic

For endothermic, think of temperature (or energy) as a reactant.

Increase temperature of endothermic reaction → Increasing a reactant → Reaction shifts to right (get rid of extra reactants and make more products)

Decrease temperature of endothermic reaction → Remove a reactant → Reaction shifts to left (make more reactants)

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Temperature and Exothermic

For exothermic, think of temperature (or energy) as a product.

Increase temperature of exothermic reaction → Increasing a product → Reaction shifts to left (get rid of extra products and make more reactants)

Decrease temperature of exothermic reaction → Remove a product → Reaction shifts to right (make more products)

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Changes Having No Effect

Some changes have no effect because they do not affect the value of “Q”.

- Adding a pure solid or liquid reactant or product.
- Increasing pressure by adding an inert gas.
- Changing the volume of a reaction with an equal number of moles of gas on each side of the reaction.
- Adding a catalyst
 - A catalyst will speed up how fast equilibrium is established—but not the number of reactants and products once it's at equilibrium.



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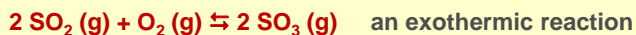
Le Chatelier's Examples

Example: Which way will the reaction shift for each of the following changes:



- | | | |
|-----------------------------|---|-------------------------------------|
| Removing NH ₄ Cl | ← | No change (it's a solid) |
| Adding HCl | ← | (Adding a product) |
| Adding Ne (g) | ← | No change (it's an inert gas) |
| Decreasing volume | ← | (Goes to side with least gas moles) |


Example: Which way will the reaction shift for each of the following changes:




- | | | |
|--------------------------|---|------------------------------------|
| Increasing volume | ← | (Goes to side with most gas moles) |
| Raising temperature | ← | (Energy is a product) |
| Adding O ₂ | → | (Adding a reactant) |
| Removing SO ₂ | ← | (Removing a reactant) |


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Free Energy





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Definition - Free Energy

Free Energy (G) – Relates temperature, enthalpy and entropy.



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Free Energy & Equilibrium

- ΔG is spontaneous, + ΔG is not spontaneous...if $\Delta G = 0$, it's at equilibrium.

Example: Find the melting point for $\text{CHCl}_3(\text{s}) \rightarrow \text{CHCl}_3(\text{l})$ if:
 $\Delta H = 9.2 \text{ kJ}$
 $\Delta S = 43.9 \text{ J/K}$

The melting point is when the "s \rightarrow l" process is at equilibrium

$\Delta H = 9.2 \text{ kJ}$
 $\Delta S = 43.9 \text{ J/K} = 0.0439 \text{ kJ/K}$
 $\Delta G = 0 \text{ kJ (at equilibrium)}$
 $T = ? \text{ K}$

$$\Delta G = \Delta H - T\Delta S$$

$$0 \text{ kJ} = 9.2 \text{ kJ} - T \times 0.0439 \text{ kJ/K}$$

$$\frac{0 \text{ kJ} - 9.2 \text{ kJ}}{-0.0439 \text{ kJ/K}} = T$$

$$T = 210 \text{ K}$$

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Free Energy & Equilibrium Constants

Free Energy can be related to the equilibrium constant.

$$\Delta G^\circ = -RT(\ln K)$$

$\Delta G^\circ = \Delta G$ (in "J") at standard state (1 atm and 1 M)
R = Gas constant (8.31 J/K \times mole)
T = Temperature (in Kelvin)
K = equilibrium constant

Example: If the equilibrium constant for a reaction is 1.74×10^{-5} , is it spontaneous at 25°C ?

$$\Delta G^\circ = -(8.31 \text{ J/K} \times \text{mole})(298 \text{ K})(\ln 1.74 \times 10^{-5})$$

$K = 1.74 \times 10^{-5}$
 $T = 25^\circ\text{C} + 273 = 298 \text{ K}$
 $\Delta G = ?$

$$\Delta G^\circ = 2.72 \times 10^4 \text{ J}$$

The reaction is not spontaneous in that direction—it will proceed in the reverse direction at this temperature—under standard conditions

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Kinetics & Equilibrium in the MCAT



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Sample Passage

Here is an example of a passage found on the MCAT

A group of students are studying the reaction $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$

Experiment 1: Students determined concentrations at equilibrium and calculated that the equilibrium constant for this reaction at 700 K is 54.

Experiment 2: Students studied reaction rates versus concentrations. Their data is represented below.

Trial	H_2	I_2	Rate
1	0.10 M	0.10 M	0.02 M/s
2	0.20 M	0.10 M	0.04 M/s
3	0.40 M	0.20 M	0.16 M/s

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Example Question - 1

1) What is the equilibrium constant at 700 K for $6 \text{ HI (g)} \rightarrow 3 \text{ H}_2 \text{ (g)} + 3 \text{ I}_2 \text{ (g)}$?

- A) 54^3
- B) 54^{-3}
- C) 54^4
- D) 54^{-4}

Find the portion of the passage that is relevant

$\text{H}_2 \text{ (g)} + \text{I}_2 \text{ (g)} \rightleftharpoons 2\text{HI (g)}$
 ... equilibrium constant for this reaction at 700 K is 54

Write the K_{eq} expression for the original reaction and the new reaction and determine their relationship

$$K_{eq\,original} = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} \quad K_{eq\,new} = \frac{[\text{H}_2]^3[\text{I}_2]^3}{[\text{HI}]^6}$$

The new expression is the reciprocal (negative exponent) and its powers have been increased by a factor of 3

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Example Question - 2

2) What is the overall order of reaction for the $\text{H}_2 + \text{I}_2 \rightarrow 2 \text{ HI}$?

- A) 0
- B) 1
- C) 2
- D) 3

Find the portion of the passage that is relevant

Trial	H_2	I_2	Rate
1	0.10 M	0.10 M	0.02 M/s
2	0.20 M	0.10 M	0.04 M/s
3	0.40 M	0.20 M	0.16 M/s

H_2 is doubled from the first trial to the second trial and the rate doubled

H_2 is first order


H_2 is doubled from the 2nd trial to the third and I_2 is also doubled while the rate goes up by a factor of 4

The doubling of H_2 would double the rate. So the doubling of I_2 is responsible for the other double ($2 \times 2 = 4$...two doublings equals $\times 4$)

H_2 and I_2 are both first order = total order of 2

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Learning Summary


The **equilibrium constant** gives the ratio of product : reactants with the stoichiometric ratios as the powers.


Kinetics is the study of the rates of reaction, which are affected by surface area, concentration, temperature and catalysts.

Le Chatelier's Principle governs how a reaction at equilibrium will change when disturbed.

Reaction mechanisms show the actual collision sequence occurring in an overall chemical reaction.

Dynamic equilibrium is established when the rates of the forward and reverse reactions are equal.

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Congratulations

You have successfully completed
the core tutorial

Kinetics & Equilibrium


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