

Chemistry 3A

Introductory General Chemistry

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Chemical Equilibrium
Collision Theory
Reaction Rates
Dynamic Equilibrium
The Equilibrium Constant
Le Chatelier's Principle
Special Types of Equilibria

Collision Theory

Collision Theory: proposes that reactant particles colliding with each other form products but under two condition

- That there is enough **kinetic energy** to cause a reaction
- That particles are in a proper orientation for a reaction to occur

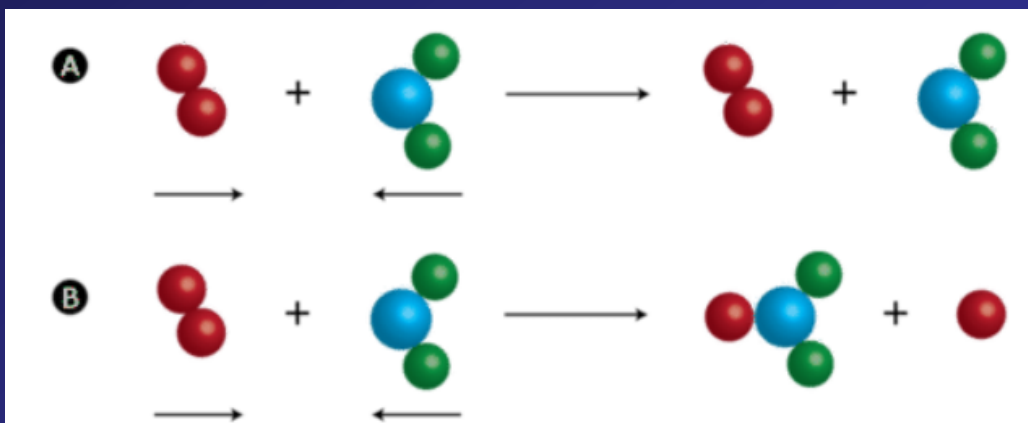


Figure 13.1.1: (A) An ineffective collision is one that does not result in product formation. (B) An effective collision is one in which chemical bonds are broken, and a product is formed.

Potential Energy Diagrams

- Also called **reaction progress curve**
- Potential energy diagrams show change in potential energy of a system as the **reactants** become **products**
- The energy change is shown by change in **enthalpy ΔH**
- If $\Delta H > 0$ (**products** higher than **reactants**), the reaction is **endothermic**. If $\Delta H < 0$, the reaction is **exothermic**

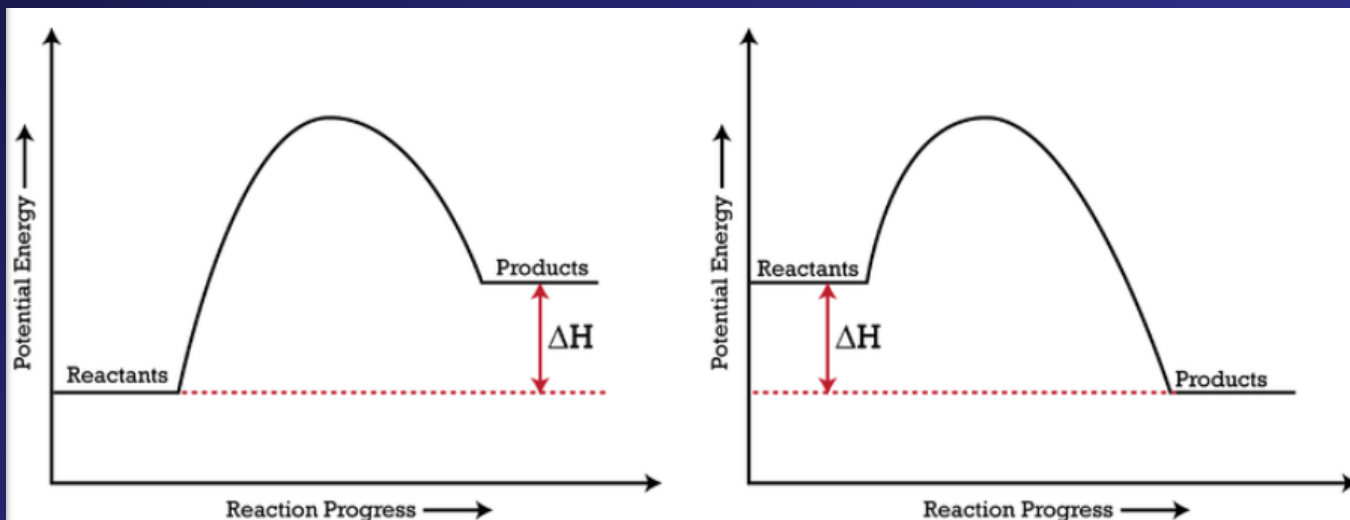
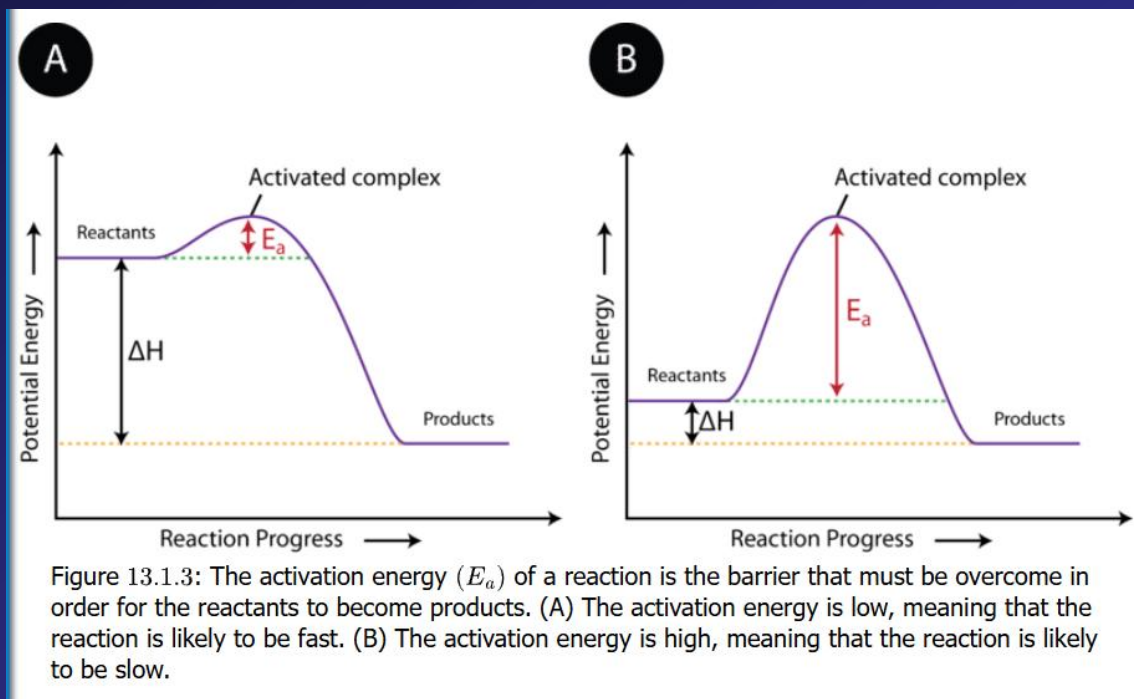


Figure 13.1.2: A potential energy diagram shows the total potential energy of a reacting system as the reaction proceeds. (Left) In an endothermic reaction, the energy of the products is greater than the energy of the reactants, and ΔH is positive. (Right) In an exothermic reaction, the energy of the products is lower than the energy of the reactants, and ΔH is negative.

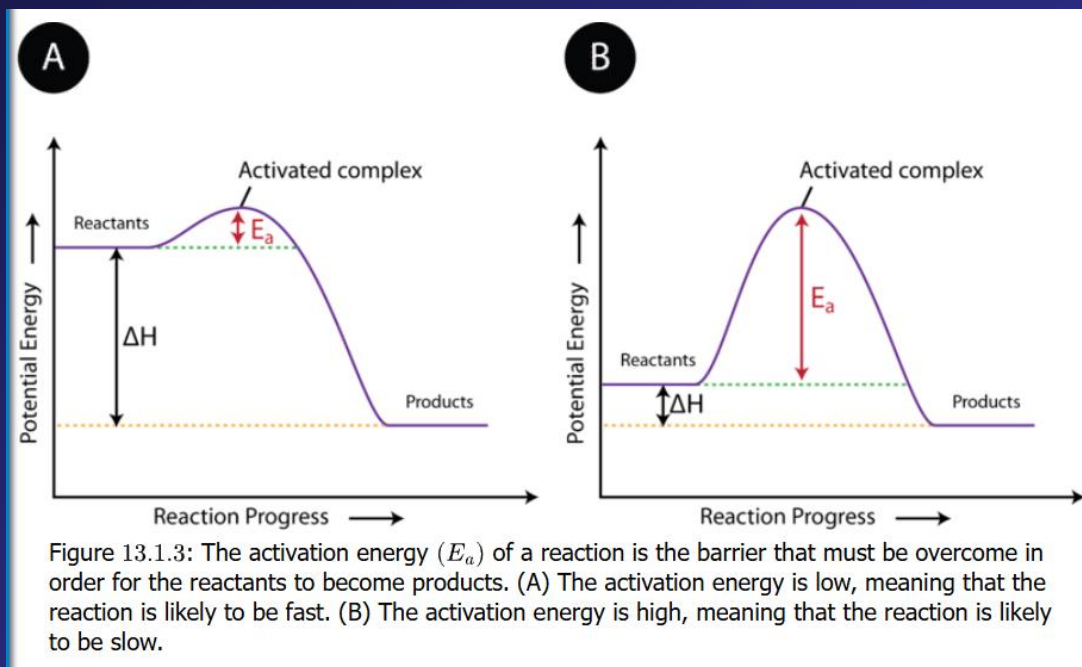
Activation Energy

- Reactant particles will collide, but not all collisions result in the chemical reaction
- But when collisions happen that have enough energy—**activation energy**—to occur, reactants will become products by forming an activated complex



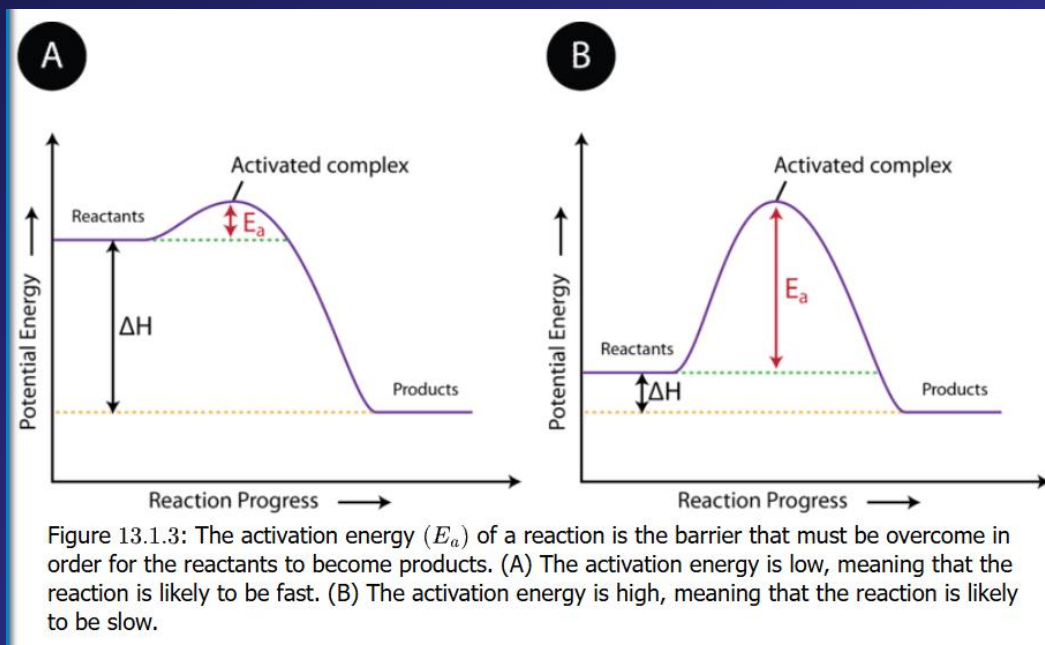
E_a for Fast or Slow Reactions

- The activation energy is symbolized as E_a
- On the reaction progress curve, it is a “hump” in the curve representing the increase in energy above the PE of the reactants, whether the reaction is endo- or exothermic
- If the hump is small, the reaction is likely to be fast. If hump is large, the reaction is likely to be slow



The Activated Complex

- When collisions lead to reactions, an **activated complex** forms as unstable arrangement of atoms that exists momentarily at the peak of the activation energy barrier
- The momentary part cannot be imagined how fast it is: **10^{-13} s** (one-tenth of a picosecond). An eye blink is one tenth of a second, so the reaction is one trillion times faster (lasers can be used to determine time)



Activated Complex Note

A note about the provided text for the course:

Book shows this visual of a reaction of $2 \text{H}_2 + \text{O}_2 \rightarrow 2 \text{H}_2\text{O}$ but that is absolutely not considered to be the mechanism of how this happens. The reaction is in fact a multi-step mechanism. The details are beyond scope of Chem 3A.

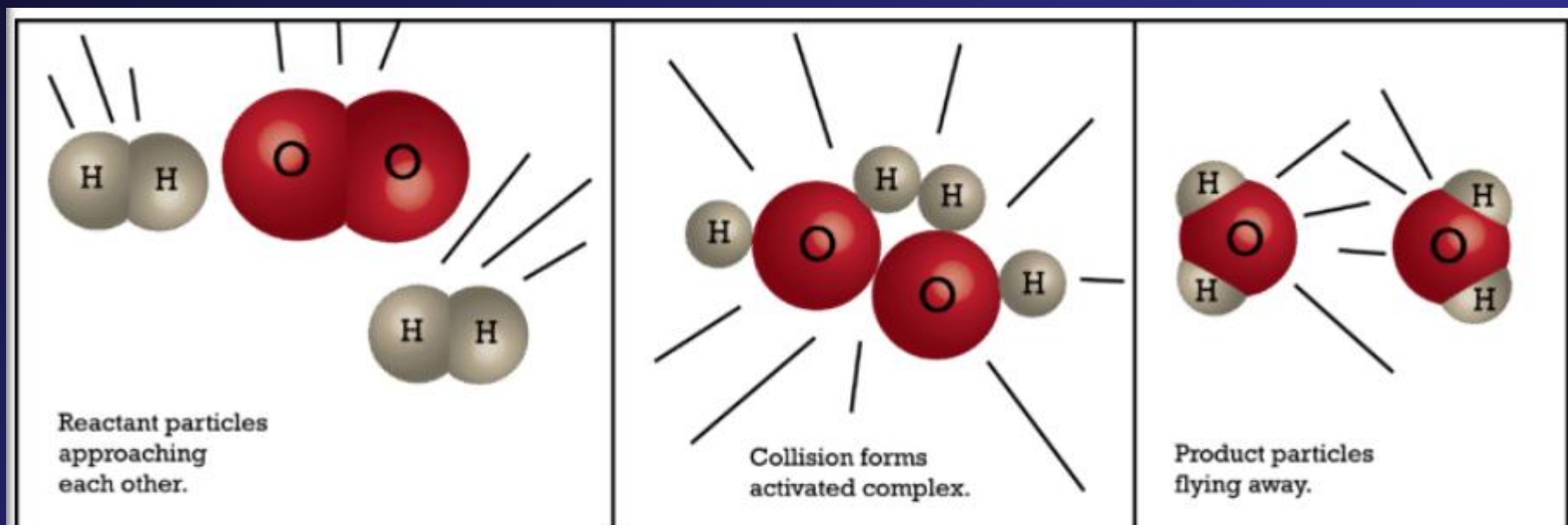


Figure 13.1.4: An activated complex is a short-lived state in which the colliding particles are at the peak of the potential energy curve.

Reaction Rates Factors: Temperature

(i) Collision frequency, (ii) collision energy, and (iii) geometric orientation are factors in a successful reaction

- Temperature affects collision frequency
- Temperature affects average velocity, and velocity is a factor in kinetic energy. Particles collide more frequently
- Temperature directly affects activation energy E_a
- Keeping environments cold versus warm versus hot is understood to control chemical reactions that, for example, might lead to preservation or spoilage of food

Concentration as a Factor

- Reactions are also affected by **concentration**
- **Higher concentrations** imply particles (molecules, etc) are closer together, more densely arranged, with a **higher probability** of **collisions**
- If a **concentration doubles**, so would the **reaction rate** also **double**
- Combustion involves a flammable substance and oxygen. If splint of wood set on fire and fire blown out, the splint continues to glow. If splint put in chamber with no O_2 , the wood stops burning (glows dissipates). But if put in 100% O_2 chamber, it burns brighter and hotter. This affects shows concentration or reactants.

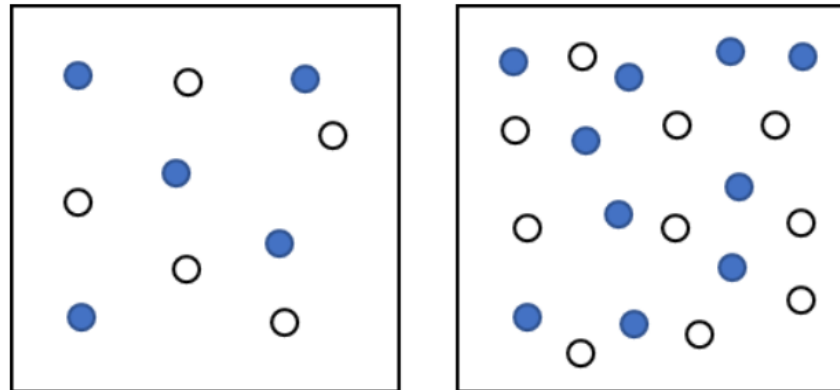


Figure 13.1.1.1: The left reaction container has a lower concentration than the right. In the right container, you can see that there are more opportunities for the reactants to collide because the concentration is higher.

Catalysis and Catalysts

- **Catalysis** is the process by which rate of chemical reaction is changed (usually increased) through the action of a **catalyst**
- A **catalyst** is a substance that increases rate of a chemical reaction without being consumed or permanently altered in the overall reaction
- The effect of catalysis is seen in the reaction progress curve as a lowering of the activation energy E_a , which enables reactants to get over the energy barrier in the reaction

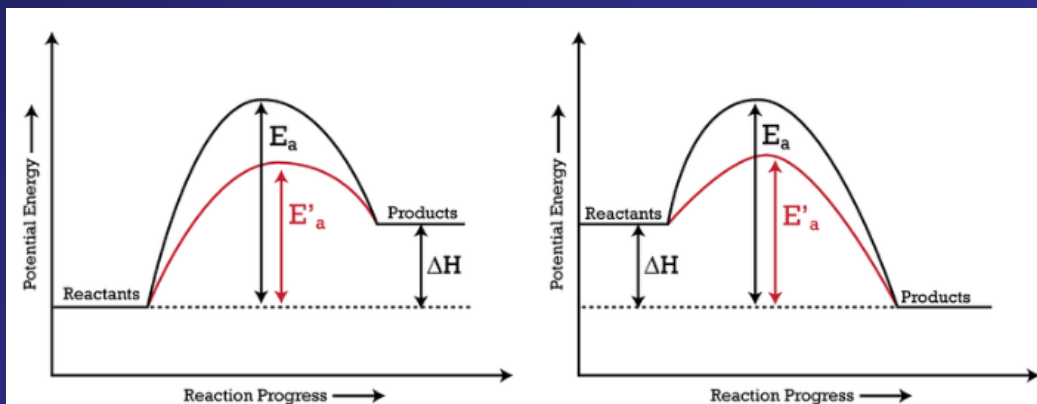
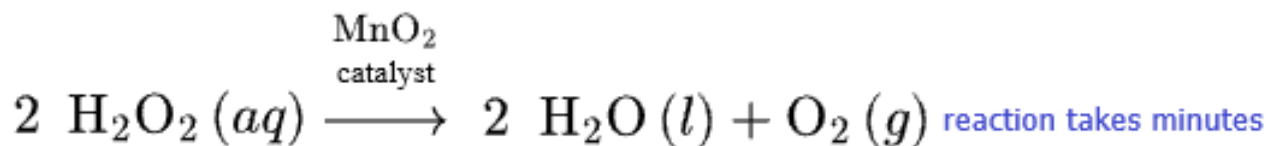
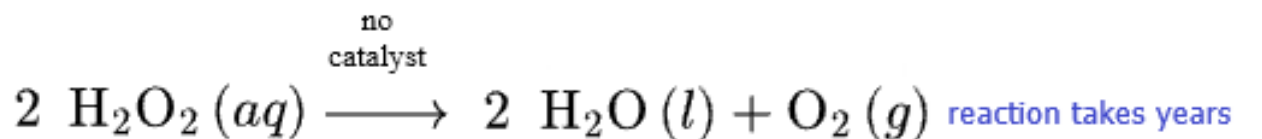


Figure 13.1.1.2: The addition of a catalyst to a reaction lowers the activation energy, increasing the rate of the reaction. The activation energy of the uncatalyzed reaction is shown by E_a , while the catalyzed reaction is shown by E'_a . The heat of reaction (ΔH) is unchanged by the presence of the catalyst.

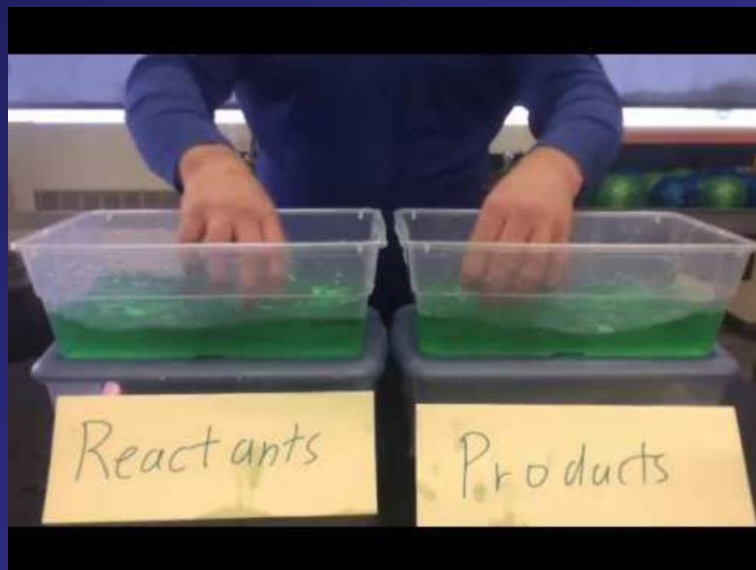
Catalysis Example

- Hydrogen peroxide (H_2O_2) is a well-known effective disinfectant. A 3% solution stores well for a few years, but it eventually degrades to water and oxygen products
- Just a small amount of manganese(IV) oxide (MnO_2) will accelerate the reaction to where it degrades within minutes



Chemical Equilibrium

- Chemical reaction rates (kinetics) were addressed in the previous slides
- This addresses the concept of chemical equilibrium, of reactants in initial conditions with no products, and of reactions showing products now becoming reactants in a reverse of the direction of the reaction



Reversible Reactions

- The \rightleftharpoons symbol/character was previously to indicate the state of **equilibrium**, the concept that **chemical reactions** often have a **forward** and **reverse** of the reaction
- The formation and decomposition of hydroiodic acid (hydrogen iodide) [HI] is an example of the reaction going both ways



Dynamic Equilibrium



- The forward and reverse directions of the reaction are shown



- N_2O_4 is colorless and NO_2 is reddish-brown so a reaction can be monitored visually
- Note that the figure shows the temperature dependence on equilibrium: at lower temperatures the formation of reactant (N_2O_4) is favored, but at higher temperatures the products will be favored



Figure 13.2.1: Dinitrogen tetroxide is a powerful oxidizer that reacts spontaneously upon contact with various forms of hydrazine, which makes the pair a popular propellant combination for rockets. Nitrogen dioxide at -196°C , 0°C , 23°C , 35°C , and 50°C . (NO_2) converts to the colorless dinitrogen tetroxide (N_2O_4) at low temperatures, and reverts to NO_2 at higher temperatures. (CC BY-SA 3.0; [Eframgoldberg](#)).

Example of Dynamic Equilibrium

- Equilibrium is shown as the change in concentration of reactant and/or product over time
- One can start with no (zero) concentration of product (for forward reaction) or of reactant (for reverse direction this become the product) and follow change in amount or concentration over time
- Eventually a plateau is reached where concentration of neither reactant or product changes
- This is **equilibrium**

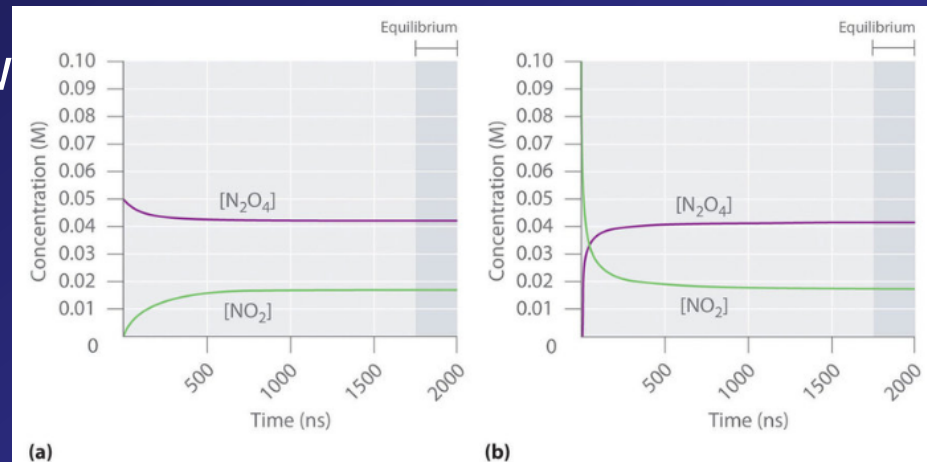


Figure 13.2.2: The Composition of $\text{N}_2\text{O}_4/\text{NO}_2$ Mixtures as a Function of Time at Room Temperature. (a) Initially, this idealized system contains 0.0500 M gaseous N_2O_4 and no gaseous NO_2 . The concentration of N_2O_4 decreases with time as the concentration of NO_2 increases. (b) Initially, this system contains 0.1000 M NO_2 and no N_2O_4 . The concentration of NO_2 decreases with time as the concentration of N_2O_4 increases. In both cases, the final concentrations of the substances are the same: $[\text{N}_2\text{O}_4] = 0.0422 \text{ M}$ and $[\text{NO}_2] = 0.0156 \text{ M}$ at equilibrium. (CC BY-SA-NC; Anonymous by request)

Change in Rate of Reaction

- In the plot shown, it shows not amount or concentration, but rather the rate of the reaction versus time. A rate of reaction is the function of the concentration (molar, M) per unit time
- Initially the sample is pure red-brown NO_2 and will form colorless N_2O_4
- As N_2O_4 product forms, the rate slows and eventually levels off to a constant rate while the reverse reaction increases to a level rate as well

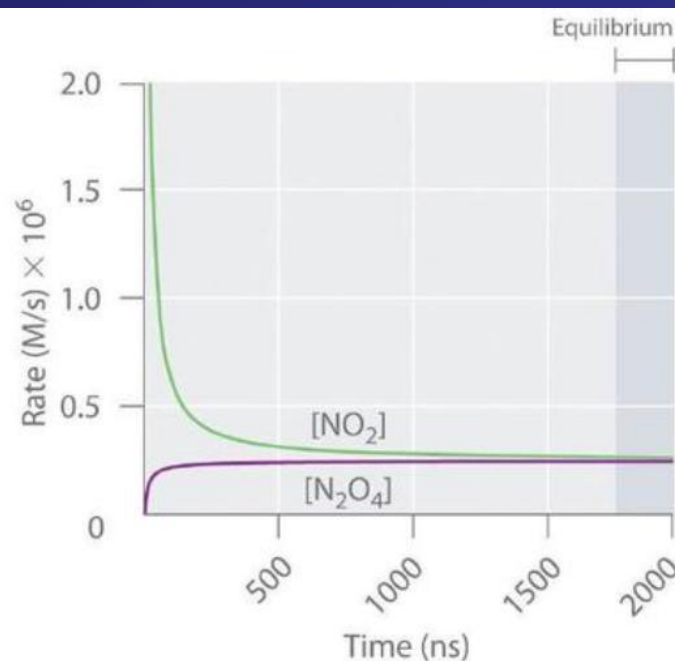
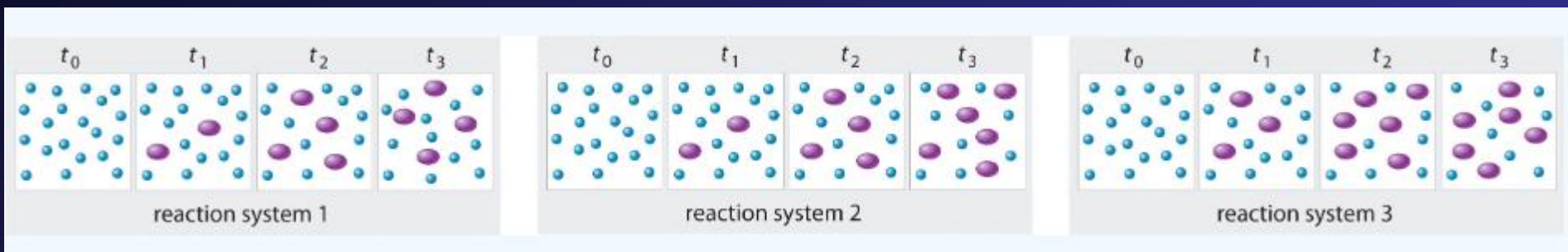


Figure 13.2.3: The Forward and Reverse Reaction Rates as a Function of Time for the $\text{N}_2\text{O}_{4(g)} \rightleftharpoons 2\text{NO}_{2(g)}$ System Shown in Part (b) in Figure 13.2.2. (CC BY-SA-NC; Anonymous by request)

Practice: Equilibrium

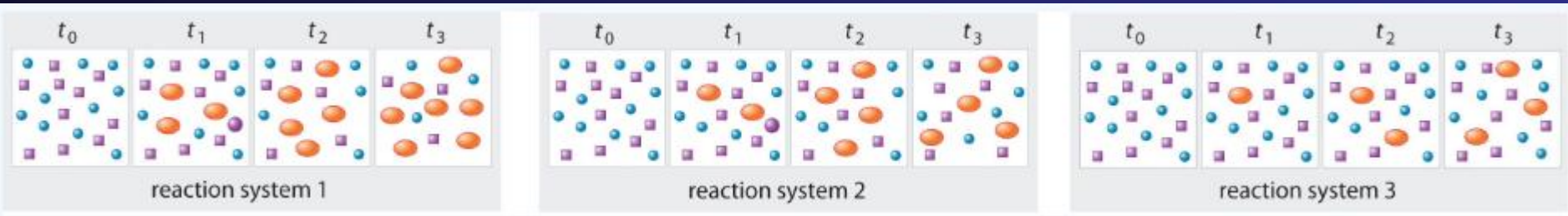
In the illustrated three reaction systems, what is the relative time to reach chemical equilibrium where $2 A \rightleftharpoons B$? A=small blue dot, B = large purple dot



- Systems 1 and 3 show **A** decrease from t_0 to t_2 , with t_2 and t_3 having no change; thus at equilibrium by t_3
- System 2: **A** and **B** still changing between t_2 and t_3 , and this system may not have reached equilibrium

Practice: Equilibrium

Another three reaction systems shown, where $A + B \rightleftharpoons C$ which system(s) has reached equilibrium?
A=blue circles, B = purple squares, C=orange ovals



System 2: the t_2 and t_3 time frames have 4 orange ovals and the count of the reactants should be same

The other systems would need to reflect no changes between the last two time frames to demonstrate equilibrium, and they do not.

Equilibrium Constant Equation

Studies of chemical reactions with forward and reverse directions showed this pattern



The equilibrium can be expressed as a constant in this equation, known as the **law of mass action**

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

Features of equation

- **K** is temperature-dependent!
- Products are in numerator, reactants are in denominator
- Brackets express concentration in molarity (units = molar)
- Expression is a quotient of products (multiplied factors)
- Coefficients of reaction are exponents in the expression (if coefficient = 1, no exponent needed)
- Solids, liquids, solvents have value = 1, so they have no effect on equation

Meaning of Equilibrium Constant

- Base on the definition of the equilibrium constant, it can be inferred that a $K > 10^3$ would indicate that the products are highly favored to the reactants in a reaction that is reversible
- The formation of HCl (g) from $\text{H}_2 \text{ (g)} + \text{Cl}_2 \text{ (g)}$ has a $K \sim 10^{33}$ at room temperature (300 K): Cl_2 is a very good oxidizer and H_2 a very good reducer
- By contrast with $K < 10^{-3}$, the reactants are highly favored

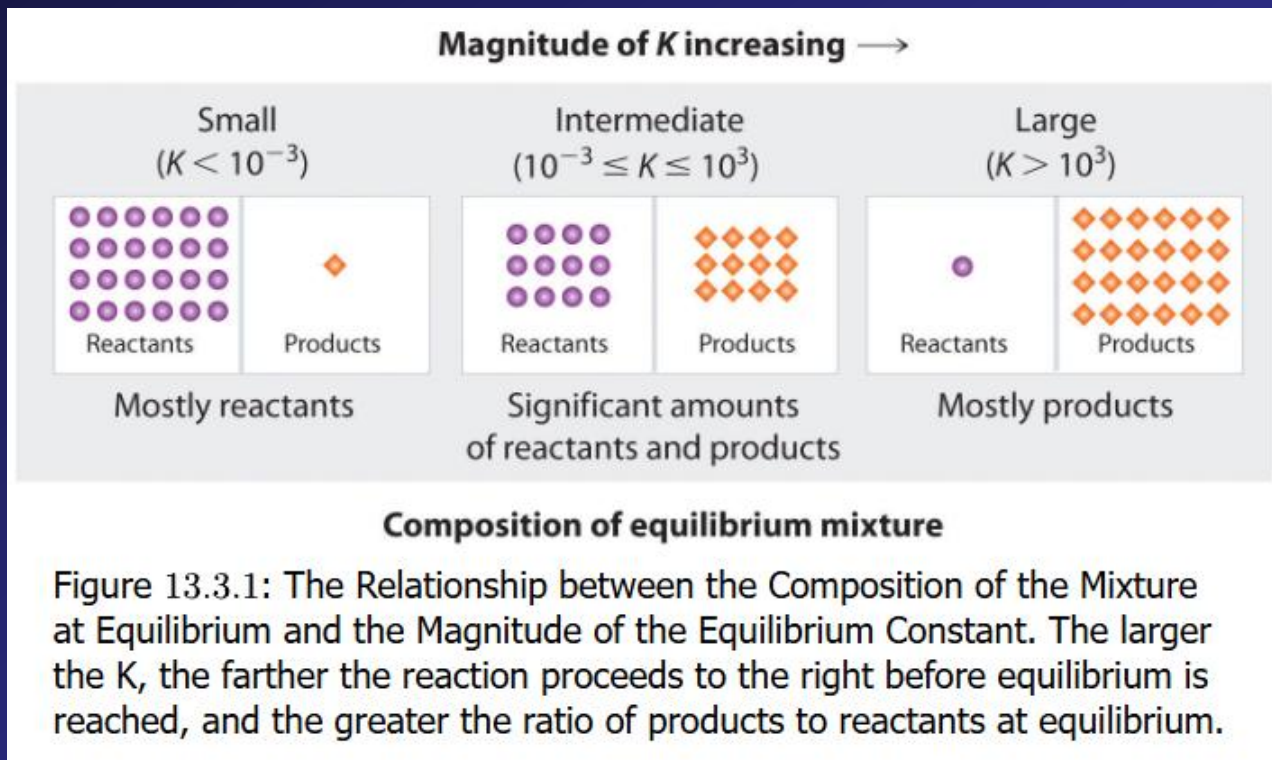
Table 13.3.1: Equilibrium Constants for Selected Reactions*

Reaction	Temperature (K)	Equilibrium Constant (K)
$\text{S (s)} + \text{O}_2 \text{ (g)} \rightleftharpoons \text{SO}_2 \text{ (g)}$	300	4.4×10^{53}
$2 \text{H}_2 \text{ (g)} + \text{O}_2 \text{ (g)} \rightleftharpoons 2 \text{H}_2\text{O (g)}$	500	2.4×10^{47}
$\text{H}_2 \text{ (g)} + \text{Cl}_2 \text{ (g)} \rightleftharpoons 2 \text{HCl (g)}$	300	1.6×10^{33}
$\text{H}_2 \text{ (g)} + \text{Br}_2 \text{ (g)} \rightleftharpoons 2 \text{HBr (g)}$	300	4.1×10^{18}
$2 \text{NO (g)} + \text{O}_2 \text{ (g)} \rightleftharpoons 2 \text{NO}_2 \text{ (g)}$	300	4.2×10^{13}
$3 \text{H}_2 \text{ (g)} + \text{N}_2 \text{ (g)} \rightleftharpoons 2 \text{NH}_3 \text{ (g)}$	300	2.7×10^8
$\text{H}_2 \text{ (g)} + \text{D}_2 \text{ (g)} \rightleftharpoons 2 \text{HD (g)}$	100	1.92
$\text{H}_2 \text{ (g)} + \text{I}_2 \text{ (g)} \rightleftharpoons 2 \text{HI (g)}$	300	2.9×10^{-1}
$\text{I}_2 \text{ (g)} \rightleftharpoons 2 \text{I (g)}$	800	4.6×10^{-7}
$\text{Br}_2 \text{ (g)} \rightleftharpoons 2 \text{Br (g)}$	1000	4.0×10^{-7}
$\text{Cl}_2 \text{ (g)} \rightleftharpoons 2 \text{Cl (g)}$	1000	1.8×10^{-9}
$\text{F}_2 \text{ (g)} \rightleftharpoons 2 \text{F (g)}$	500	7.4×10^{-13}

*Equilibrium constants vary with temperature. The K values shown are for systems at the indicated temperatures.

Meaning of Range of K

Practical meaning of the **equilibrium constant K** is to indicate whether a reaction at the particular **temperature** and **some other conditions** will favor reactants not forming products ($K < 10^{-3}$), or the reaction going to completion to products ($K > 10^3$), or an equilibrium reached where there is an even mixture of reactants and products ($10^{-3} \leq K \leq 10^3$)

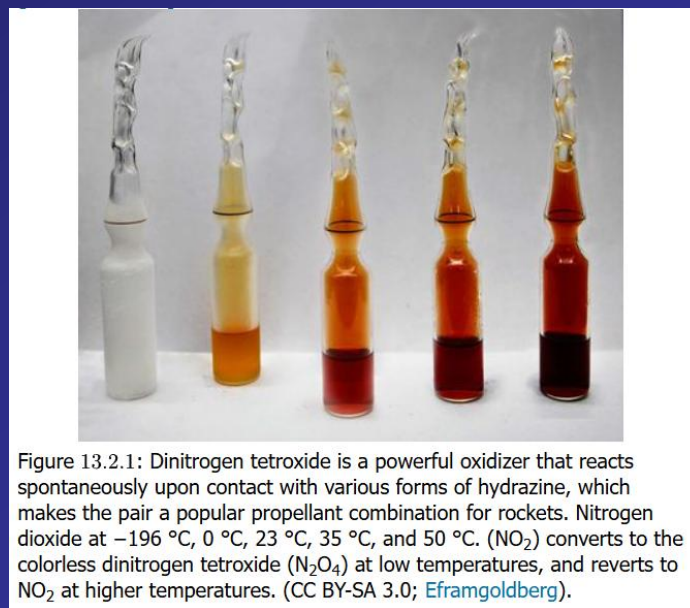
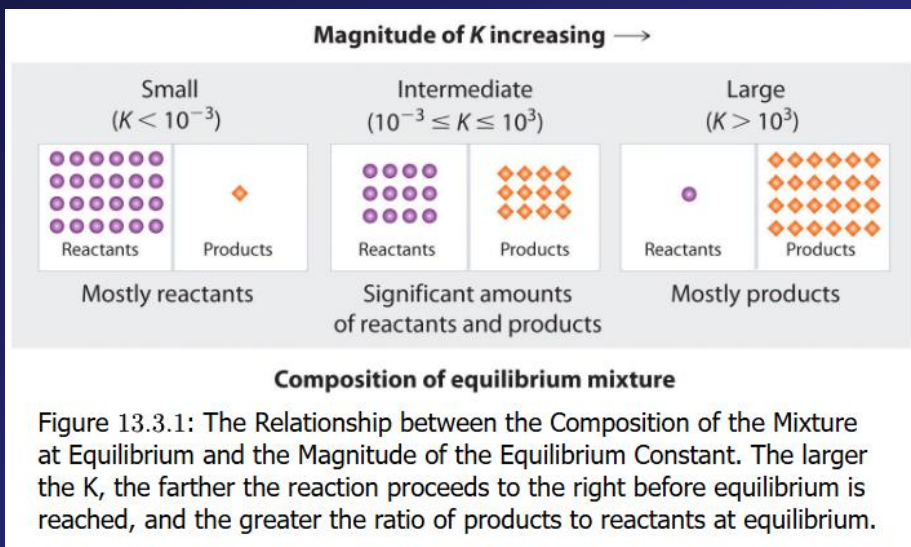


Example: Meaning of Range of K

Recall the reactions: [colorless] $\text{N}_2\text{O}_4(g) \rightleftharpoons 2 \text{NO}_2(g)$ [red–brown]

Here is the table of K values for that reaction to emphasize the point

Temperature T	K_p	Shift in Equilibrium	Observation
100°C (~373 K)	1.3×10^6	product NO_2 strongly favored	relatively dark brown
25°C (298 K)	~58	N_2O_4 favored	brown
0°C (273 K)	0.113-0.142	both significantly present	pale brown or nearly colorless
-78°C (195 K)	0.066	reactant N_2O_4 favored	colorless



Practice: Equilibrium Constant Expression

Write the equilibrium constant expression for the balanced reactions (chemical equations)



$$\frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3}$$



$$\frac{[\text{CO}_2]}{[\text{CO}][\text{O}_2]^{1/2}}$$



$$\frac{[\text{CO}]^2[\text{O}_2]}{[\text{CO}_2]^2}$$

Practice: Equilibrium Constant

Write the equilibrium constant (not the equilibrium constant expression) for the balanced reactions (chemical equations)



$$K = \frac{[\text{N}_2][\text{O}_2]^{1/2}}{[\text{N}_2\text{O}]}$$



$$K = \frac{[\text{CO}_2]^{16}[\text{H}_2\text{O}]^{18}}{[\text{C}_8\text{H}_{18}]^2[\text{O}_2]^{25}}$$



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

Practice: Predicting What Predominates

Predict if a system has only products, only reactants, or appreciable amounts of reactants and products



Will substantially have mix of products and reactants



Strongly favors reactant formation and little products



Substantial presence of both reactants and products



Favors products, forward reaction to completion

Practice: Temperature and K

At which temperature would you expect to find highest proportion of H_2 and N_2 at equilibrium? The balanced chemical equation is:



The equilibrium constants for this are shown at the different temperatures:

- $K_{25^\circ\text{C}} = 3.3 \times 10^8$
- $K_{177^\circ\text{C}} = 2.6 \times 10^3$
- $K_{327^\circ\text{C}} = 4.1$

The question asks under what conditions the reactants would be favored and product formation is less favored. To favor reactants, K should decrease. From the series of K values, it is clear that as the temperature goes higher, K decreases. So a higher temperature would favor reactants. A temperature of 327°C is best.

Practice: Calculating K

Given the following reaction



The following concentrations were found at equilibrium:

- $[\text{SO}_2] = 1.20 \text{ M}$
- $[\text{NO}_2] = 0.60 \text{ M}$
- $[\text{NO}] = 1.6 \text{ M}$
- $[\text{SO}_3] = 2.2 \text{ M}$
- Calculate the value of K

To calculate, you first have to set up the equilibrium constant expression

$$K = \frac{[\text{SO}_3][\text{NO}]}{[\text{SO}_2][\text{NO}_2]}$$

Then substitute the values and solve

$$K = \frac{(2.2)(1.6)}{(1.20)(0.60)} = 4.9$$

Practice: Calculating K

Given the following reaction



The following concentrations were found at equilibrium:

- $[\text{SO}_2] = 0.90 \text{ M}$
- $[\text{O}_2] = 0.35 \text{ M}$
- $[\text{SO}_3] = 1.1 \text{ M}$

Calculate the value of K

To calculate, you first have to set up the equilibrium constant expression

$$K = \frac{[\text{SO}_3]^2}{[\text{SO}_2]^2[\text{O}_2]}$$

Then substitute the values and solve

$$K = \frac{(1.1)^2}{(0.90)^2(0.35)} \sim 4.3$$

Notation of Temperature on K

- It should re-emphasized that K is temperature-dependent
- Because of this, K is often specified with a temperature that can be in Kelvin or Celsius
- It may be specified as a subscript or in parenthesis

$K_{298\text{K}}$

$K(700\text{K})$

$K_{25^\circ\text{C}}$

$K_c(150^\circ\text{C})$ equilibrium of concentrations

$K_p(500\text{K})$ equilibrium of partial pressures of gases

Le Chatelier's Principle

- 1884: Le Chatelier reports that when a system at equilibrium is disturbed/stressed, the system will respond/adjust to restore the equilibrium
- Stresses/disturbances include
 - Changing concentrations of reactants and/or products such as adding more or removing some of a reactant or product
 - Changing the temperature of the system: this changes equilibrium constant K
 - Changing the pressure in the system: this can affect partial pressures of gases that are reactants and/or products. It can also effect the enthalpy ΔH that controls the PE vs reaction progress plot

Original Equilibrium	Favored Reaction	Result
$A \rightleftharpoons B$	Forward: $A \rightarrow B$	$[A]$ decreases; $[B]$ increases
$A \rightleftharpoons B$	Reverse: $A \leftarrow B$	$[A]$ increases; $[B]$ decreases



Figure 9.6.1: Henri Le Chatelier.

Concentration “Stress”

Effective illustration is production of ammonia by Haber-Bosch process



- If more N_2 added, forward reaction favored
- More product is formed, and the other reactant H_2 is additionally consumed (see plot)

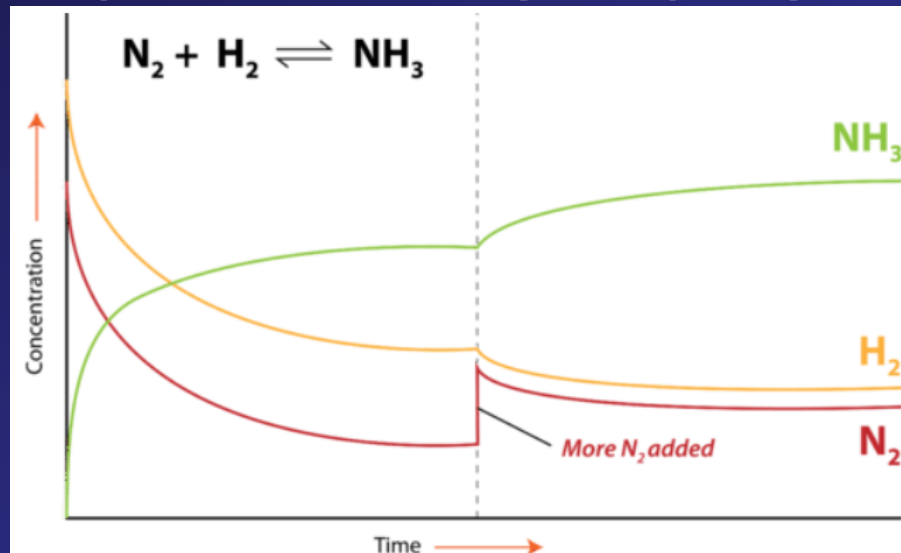


Figure 9.6.2: The Haber-Bosch process is an equilibrium between reactants N_2 and H_2 and product NH_3 .

Concentration “Stress”

This principle makes it possible to predict the shift of the reaction—forward or reverse—occurs to make an adjustment to restore equilibrium

Table 9.6.1

Stress	Response
addition of reactant	forward reaction favored
addition of product	reverse reaction favored
removal of reactant	reverse reaction favored
removal of product	forward reaction favored

Predict what happens with the $\text{N}_2 + 3 \text{H}_2 \rightleftharpoons 2 \text{NH}_3$

- H_2 is added

More H_2 reactant, shift to right to products (forward reaction)

- NH_3 is added

More NH_3 product, shift to left to reactants (reverse reaction)

- NH_3 is removed

Less NH_3 product, shift to right to products (forward reaction)

Practice: Concentration “Stress”

Predict what happens with the following reaction



- Br_2 is removed

Less Br_2 reactant,
shift to left to reactants (reverse reaction)

- COBr_2 is added

More COBr_2 product,
also shift to left to reactants (reverse reaction)

Temperature “Stress”

- Returning to the ammonia production, the **thermochemical equation** is shown
 - recall it includes a positive or negative energy value: if positive, heat is released (exothermic), if negative, heat/energy is required (endothermic)
 - The forward reaction is positive so heat released
 - The reverse reaction therefore requires energy



What effect temperature?

- Reducing temperature has effect of removing energy/heat, which favors products
- Adding heat (raising temperature) would favor going in reverse reaction, forming reactants

Temperature “Stress”

- Raising temperature has effect of favoring the direction of the reaction that requires heat/energy to form the compounds
- If the direction of a reaction is endothermic (requires heat/energy), raising temperature pushes the reaction in the endothermic direction
- The logic applies that if a reaction is exothermic (releases heat/energy), then lowering temperature should favor the reaction towards the exothermic direction

Practice: Temperature “Stress”

- Predict the effect to increasing temperature:



The reaction is exothermic, release heat/energy. Lowering temperature would promote the forward reaction. Increasing temperature would provide energy to promote the reverse reaction: so the reverse reaction is favored

- Predict the effect to decreasing temperature:



The reaction is endothermic, release heat/energy. Lowering temperature would promote the reverse reaction since the heat/energy is taken away. Increasing temperature would provide energy to promote the forward reaction: so the reverse reaction is favored

Pressure “Stress”

- When the reactants and products are gases, changes in the partial pressure of any component of the system would require restoration of the equilibrium

This would not be true for solids and liquids

- A in figure shows system at equilibrium
- In B, pressure is increased (out of equilibrium)
- In C, equilibrium restored

What happened?



With increased pressure, whichever side has fewer moles of all gases will be favored. 4 moles of gas on reactants form 2 moles of gas in products, so higher pressure pushes to 2 moles

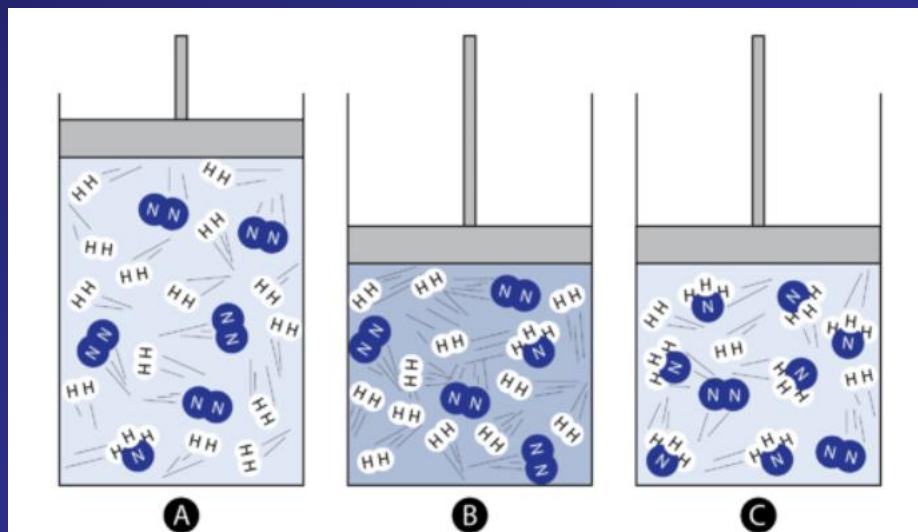


Figure 9.6.3: Effect of pressure on equilibrium. (A) is at equilibrium, (B) increase of pressure through decreased volume, and (C) equilibrium is reestablished.

Practice: Pressure “Stress”

Stress	Response
pressure increase	reaction produces fewer gas molecules
pressure decrease	reaction produces more gas molecules

- Predict what happens with pressure changes in this reaction



O_2 is the only gas in the reaction. So increasing pressure should favor side with fewer moles of gas, in this case, the reactants side, which has no gas actually!

- Predict what happens with pressure changes in this reaction



The reactants show two moles of gas (one each of H_2 and Cl_2). The products are 2 moles of one gas, HCl . Changing pressure is unlikely to have an effect on the forward or reverse reaction

- Predict what happens with pressure is decreased



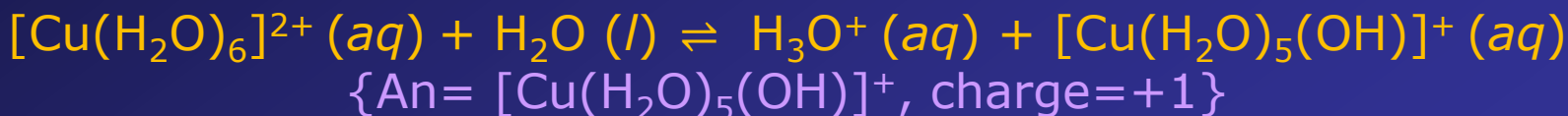
Favors side with MORE moles: toward reverse (left) to reactants

Patterns in Acid-Base Reactions

- Acids and bases in aqueous solution will react with the following patterns



- For the acid reaction, HAn refers to the acid as a proton donor, and An to what is the conjugate base (review that unit). When the proton is donated to the proton acceptor, namely the base, An is the species that has basically lost a proton and its charge will be “less positive by 1”. What does that mean? All these reactions below are acids donating a hydrogen ion to water as a base:



- All those patterns show donation of a hydrogen ion, H^+ , and the conjugate base being reduced in charge by the charge of a hydrogen ion, which is +1

Patterns in Acid-Base Reactions

- For base reactions:



- For the **base reaction**, **An** refers to the **base** as a **proton acceptor**, and **HAn** is the **conjugate acid** (review that unit). When the **proton** is **taken** from the **proton donor**, namely the acid, **HAn** is the species that has basically gained a proton and its charge will be “more positive by 1”. What does that mean? All these reactions below are bases taken a proton from water acting as an acid:



- All those patterns show gaining a hydrogen ion, H^+ , and the conjugate acid being increased in charge by the charge of a hydrogen ion, which is +1. And often it is typically H_2O acting the as an acid when a base is added, so a proton is taken from it leaving OH^- as the species. Bases increase the $[\text{OH}^-]$ concentration, so this is a classic pattern.

K Expressions for Acids and Bases

- Acids and bases in aqueous solution will react with the following patterns



- Now apply the definition of the equilibrium constant equation to the equilibrium reaction:

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{An}^-]}{[\text{HAn}]}$$

- Two things to note here
 - The constant K_a is called the **acid dissociation constant**. It is an **equilibrium constant** like all others, but just specifically indicates with the subscript "a" that it refers to an acid giving its proton (hydrogen ion, H^+) to a base, typically H_2O (because it's in aqueous solution), acting as a base [proton acceptor] in the reaction
 - H_2O (water) is excluded as a reactant in the K_a expression as it will not influence the equilibrium. [Recall the condition of excluding compounds in "(l)" state]

K Expressions for Acids and Bases

- The K_a expression for a strong acid HCl was shown. What about a strong base like NaOH?



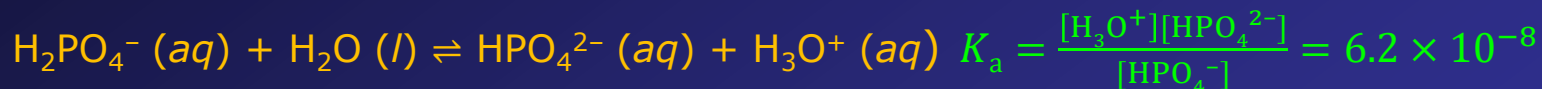
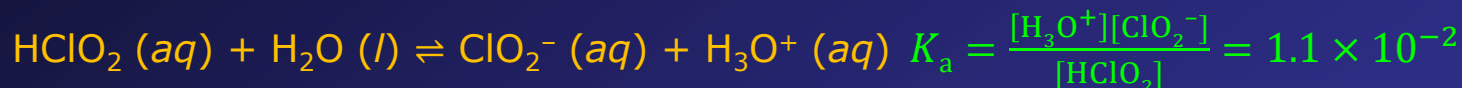
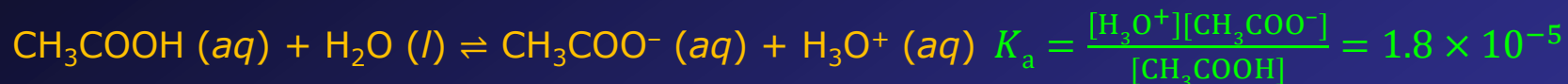
- Now apply the definition of the equilibrium constant equation to the equilibrium reaction:

$$K_b = \frac{[\text{HAn}^+][\text{OH}^-]}{[\text{An}]}$$

- Two things to note here
 - The constant K_b is called the **base ionization constant** (not **base dissociation constant!!**) It too is an **equilibrium constant** like all others, but the subscript "b" that it refers to an acid giving its proton (hydrogen ion, H^+) to a base, typically H_2O (because it's in aqueous solution), acting as a base [proton acceptor] in the reaction
 - H_2O (water) is excluded as a reactant in the K_b expression as it will not influence the equilibrium. [Recall the condition of excluding compounds in "(l)" state]

Tying Together Use of Acid-Base K Expressions

- The 4 previous slides go into extraordinary detail (that is, with examples) to try to make sense of the textbook's use of acid and base equilibrium constant expressions
- You should be able to apply definition for K expressions for weak acids like those below. The first three are:



Acid	K_a
$\text{HC}_2\text{H}_3\text{O}_2$	1.8×10^{-5}
HClO_2	1.1×10^{-2}
H_2PO_4^-	6.2×10^{-8}
HCN	6.2×10^{-10}
HF	6.3×10^{-4}
HNO_2	5.6×10^{-4}
H_3PO_4	7.5×10^{-3}

Tying Together Use of Acid-Base K Expressions

- Another thing you should be able to understand from the equilibrium constants for the weak acids in particular
- In the table below, which is the weakest of the weak acids?

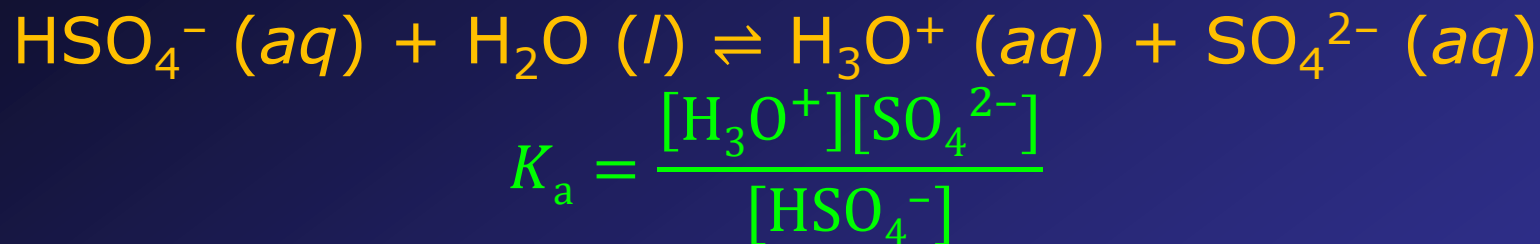
Recall that the acid dissociation constant is an equilibrium constant with an expression $K_a = \frac{[\text{Products}]}{[\text{Reactants}]}$ which is multiplication of product concentrations

divided by multiplication reactant concentrations. If the K_a is larger, that means the acid is stronger in protonating the other reactant (the proton acceptor). If K_a is smaller, the acid is less likely to protonate. The meaning of that is that it would be the weaker of weak acids: less likely to dissociate, less likely to be a proton donor. In that list, that looks like HCN: $\text{HCN} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{CN}^-$

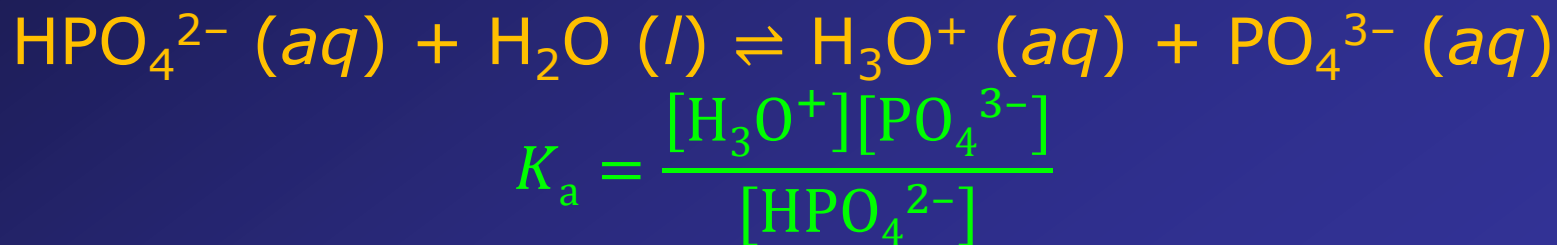
Acid	K_a
$\text{HC}_2\text{H}_3\text{O}_2$	1.8×10^{-5}
HClO_2	1.1×10^{-2}
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HCN	6.2×10^{-10}
HF	6.3×10^{-4}
HNO_2	5.6×10^{-4}
H_3PO_4	7.5×10^{-3}

Practice: Equilibrium Equations for K_a

Write the chemical equilibrium equation and the K_a expression for weak acid HSO_4^-



Do the same for the weak acid HPO_4^{2-}



Water as Acid & Base: $K_w = K_a K_b$

Previously we showed the generic equilibrium constant equation for K_a and K_b . (It can be shown that $\text{HAn} = \text{HAn}^+$ and $\text{An}^- = \text{An}$ as corresponding conjugate acids and bases)

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{An}^-]}{[\text{HAn}]}, \quad K_b = \frac{[\text{HAn}][\text{OH}^-]}{[\text{An}^-]}$$

Doing some algebra to solve for HAn on K_a and K_b ,

$$[\text{HAn}] = \frac{[\text{H}_3\text{O}^+][\text{An}^-]}{K_a}, \quad [\text{HAn}] = \frac{K_b[\text{An}^-]}{[\text{OH}^-]}$$

And so

$$\frac{[\text{H}_3\text{O}^+][\text{An}^-]}{K_a} = \frac{K_b[\text{An}^-]}{[\text{OH}^-]}$$

Getting the constants on one side of the equation and canceling out $[\text{An}^-]$:

$$[\text{H}_3\text{O}^+][\text{OH}^-] = K_a K_b$$

Since $K_w = [\text{H}_3\text{O}^+][\text{OH}^-]$, therefore $K_w = K_a K_b$

And since $K_w = 1.0 \times 10^{-14}$, then $K_a K_b = 1.0 \times 10^{-14}$

Equilibrium Reaction of Precipitation

- Up to this point, precipitation reactions usually involving some metal cation (M^+) and a nonmetal monatomic or polyatomic anion (X^-) would be described by this reaction pattern:



- But precipitation reactions are not actually one way—towards the formation of a solid precipitate
- Just like many chemical reactions, they are two-way, reversible: if the well-known precipitant silver chloride ($AgCl$) is spooned out as a solid into a beaker of water, the aqueous solution will have detectable levels of Ag^+ and Cl^- ions
- It's all about a range of solubility, from very low to super high (total dissolution)

The Solubility Product K_{sp}

- The precipitation reaction is properly written with the equilibrium character



- And when written this way



the equilibrium equation is

$$K_{sp} = [M^{y+}]^n [X^{n-}]^y$$

- Notes
 - K_{sp} is the **solubility product constant**
 - This template/pattern covers all conditions for the charge state (± 1 , ± 2 , etc) of M and X and their coefficients
 - Always remember that for all equilibrium constant expressions that coefficients in the K equation are shown as exponents to the concentration of the species
 - Reactants are shown in denominator of K equations, but since reactant MX is a solid, it will not be in K_{sp} equations typically

Example K_{sp} Values

- The silver chloride solubility chemical reaction is this



Table below the reactions and equilibrium constant equations

Compound	Reaction	K_{sp}
Ag_2SO_4	$\text{Ag}_2\text{SO}_4 (s) \rightleftharpoons 2 \text{Ag}^+ (aq) + \text{SO}_4^{2-} (aq)$	$[\text{Ag}^+]^2[\text{SO}_4^{2-}] = 1.5 \times 10^{-5}$
$\text{Ca}(\text{OH})_2$	$\text{Ca}(\text{OH})_2 (s) \rightleftharpoons \text{Ca}^{2+} (aq) + 2 \text{OH}^- (aq)$	$[\text{Ca}^{2+}][\text{OH}^-]^2 = 5.0 \times 10^{-6}$
AgCl	$\text{AgCl} (s) \rightleftharpoons \text{Ag}^+ (aq) + \text{Cl}^- (aq)$	$[\text{Ag}^+][\text{Cl}^-] = 1.8 \times 10^{-10}$
BaSO_4	$\text{BaSO}_4 (s) \rightleftharpoons \text{Ba}^{2+} (aq) + \text{SO}_4^{2-} (aq)$	$[\text{Ba}^{2+}][\text{SO}_4^{2-}] = 1.1 \times 10^{-10}$
$\text{Mg}(\text{OH})_2$	$\text{Mg}(\text{OH})_2 (s) \rightleftharpoons \text{Mg}^{2+} (aq) + 2 \text{OH}^- (aq)$	$[\text{Mg}^{2+}][\text{OH}^-]^2 = 5.6 \times 10^{-12}$
AgI	$\text{AgI} (s) \rightleftharpoons \text{Ag}^+ (aq) + \text{I}^- (aq)$	$[\text{Ag}^+][\text{I}^-] = 8.5 \times 10^{-17}$
HgI_2	$\text{HgI}_2 (s) \rightleftharpoons \text{Hg}^{2+} (aq) + 2 \text{I}^- (aq)$	$[\text{Hg}^{2+}][\text{I}^-]^2 = 2.9 \times 10^{-29}$
$\text{Ca}_3(\text{PO}_4)_2$	$\text{Ca}_3(\text{PO}_4)_2 (s) \rightleftharpoons 3 \text{Ca}^{2+} (aq) + 2 \text{PO}_4^{3-} (aq)$	$[\text{Ca}^{2+}]^3[\text{PO}_4^{3-}]^2 = 2.1 \times 10^{-33}$