Chemistry 120 Fall 2016

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Test Dates:

September 23, **2016 (Test 1): Chapter 1,2 &3**
October 13, **2016 (Test 2): Chapter 4 & 5**
October 31, **2016 (Test 3): Chapter 6, 7 & 8**
November 15, **2016 (Test 4): Chapter 9, 10 & 11**
November 17, **2016 (Make-up test) comprehensive: Chapters 1-11**

Chapter 9. Chemical Reactions

9-1 Types of Chemical Reactions

- Combination Reactions
- Decomposition Reactions
- Displacement Reactions
- Exchange Reactions
- Combustion Reactions

9-2 Redox and Nonredox Chemical Reactions

9-3 Terminology Associated with Redox Processes

- Oxidizing Agents and Reducing Agents

9-4 Collision Theory and Chemical Reactions

- Molecular Collisions
- Activation Energy
- Collision Orientation

Chapter 9. Chemical Reactions

Topics we’ll be looking at in this chapter

- Types of chemical reactions
- Redox and non-redox reactions
- Terminology associated with redox processes
- Collision theory and chemical reactions
- Exothermic and endothermic reactions
- Factors that influence chemical reaction rates
- Chemical equilibrium
- Equilibrium constants
- Altering equilibrium conditions: Le Chatelier

Types of chemical reactions

- A chemical reaction is a process in which at least one new substance is produced as a result of a chemical change.
- Chemical reactions usually take the form of one the following basic types:
  - Combination reactions
  - Decomposition reactions
  - Single-replacement reactions
  - Double-replacement reactions
  - Combustion reactions

Types of chemical reactions

- A combination reaction is a chemical reaction in which a single product is produced from two (or more) reactants.

$$X + Y \rightarrow XY$$

- Real examples:

$$\left.\begin{array}{l} \mathrm{Ca} + \mathrm{S} \rightarrow \mathrm{CaS} \\ N_2 + 3H_2 \rightarrow 2NH_3 \\ 2Na + O_2 \rightarrow Na_2O_2 \end{array}\right\} \text{Examples involving the combination of two elements to yield a single product}$$

$$\left.\begin{array}{l} SO_3 + H_2O \rightarrow H_2SO_4 \\ 2NO + O_2 \rightarrow 2NO_3 \\ 2NO_2 + H_2O_2 \rightarrow 2HNO_3 \end{array}\right\} \text{Examples involving the combination of two compounds to yield a single product}$$

Types of chemical reactions

- A decomposition reaction is a chemical reaction in which a single reactant is converted into two or more products (these can be elements or compounds)

$$XY \rightarrow X + Y$$

- Decomposition to elements tends to occur at very high temperatures:

$$\left.\begin{aligned} &2CuO \rightarrow 2Cu + O_2 \\ &2H_2O \rightarrow 2H_2 + O_2 \end{aligned}\right\} \text{Elements generated by decomposition}$$

- At lower temperatures, decomposition to other compounds tends to occur

$$\left.\begin{aligned} &CaCO_3 \rightarrow CaO + CO_2 \\ &2KClO_3 \rightarrow 2KCl + 3O_2 \\ &4HNO_3 \rightarrow 4NO_2 + 2H_2O + O_2 \end{aligned}\right\} \begin{array}{l}\text{Stable compounds may also be} \\ \text{produced, generally at lower} \\ \text{temperatures}\end{array}$$

Types of chemical reactions

- Single-replacement reactions are reactions in which an atom or molecule replaces another atom or group of atoms from a second reactant

$$X + YZ \rightarrow Y + XZ$$

$$\left.\begin{array}{l} Fe + CuSO_4 \rightarrow Cu + FeSO_4 \\ Mg + Ni(NO_3)_2 \rightarrow Ni + Mg(NO_3)_2 \\ Cl_2 + NiI_2 \rightarrow I_2 + NiCl_2 \end{array}\right\} \text{Elements replacing other elements}$$

$$\left. 4PH_3 + Ni(CO)_4 \rightarrow 4CO + Ni(PH_3)_4 \right\} \text{Compound replacing a group of atoms}$$

Types of chemical reactions

- Double-replacement reactions are chemical reactions in which two substances exchange parts with one another, forming two different substances

$$AX + BY \rightarrow AY + BX$$

- In most cases, at least one of the products is formed in a different physical state (e.g. a solid formed after mixing two solutions)

$$\left.\begin{array}{l} AgNO_3(aq) + KCl(aq) \rightarrow KNO_3(aq) + AgCl(s) \\ 2KI(aq) + Pb(NO_3)_2(aq) \rightarrow 2KNO(aq) + PbI_2(s) \end{array}\right\}$$

One of the products is a solid

Types of chemical reactions

- Combustion reactions occur between substances and oxygen, producing an oxide product in addition to other product(s). Usually, they give off heat (sometimes light).
- Hydrocarbons (compounds that only have carbon and hydrogen in their chemical formulas) react in combustion reactions to produce CO_2 and H_2O:

$$2C_2H_2 + 5O_2 \rightarrow 4CO_2 + 2H_2O$$

$$C_3H_8 + 5O_2 \rightarrow 3CO_2 + 4H_2O$$

$$C_4H_8 + 6O_2 \rightarrow 4CO_2 + 4H_2O$$

Types of chemical reactions

- Many examples of combustion reactions exist where the reactant is not a hydrocarbon:

$$CS_2 + 3O_2 \rightarrow CO_2 + 2SO_2$$

$$2H_2S + 3O_2 \rightarrow 2SO_2 + 2H_2O$$

$$4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O$$

$$2ZnS + 3O_2 \rightarrow 2ZnO + 2SO_2$$

Magnesium ribbon burning

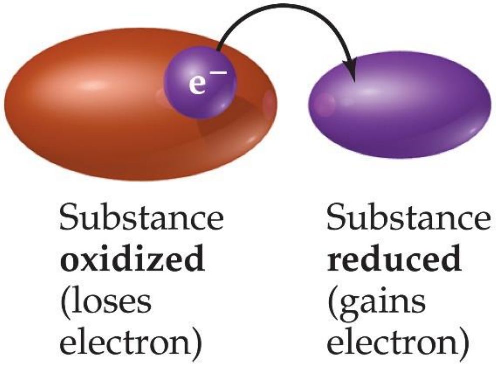
Combustion of red phosphorus

Indicators of chemical reactions

- Sometimes, it is difficult to determine whether a chemical reaction has happened or not. There are several indicators for this:
  - Production of a solid, liquid, or gas
  - Generation/consumption of heat
  - Color change
  - Production of light

Redox and non-redox chemical reactions

- The term, redox, comes from *reduction-oxidation*. These reactions involve the transfer of electrons from one reactant to another. In the course of this process:
- one reactant becomes oxidized (loses electron(s))
- one reactant becomes reduced (gains electron(s))



Can't have one without the other. The reactant that is oxidized (loses one or more electrons) loses them to the reactant that becomes reduced (gains one or more electrons)

Redox and non-redox chemical reactions

- Redox reactions involve the transfer of electrons between reactants. Non-redox reactions do not involve electron-transfer.
- We can keep track of where electrons are moving using a bookkeeping system called oxidation numbers
- Oxidation numbers represent the charges that atoms appear to have when the electrons in each bond it is participating in are assigned to the more electronegative of the two atoms involved in the bond

Redox and non-redox chemical reactions

Rules for assigning oxidation numbers

Oxidation numbers are determined for elements in formulas using a series of rules:

1. The oxidation number of an element in its elemental state is always zero
2. The oxidation number of a monatomic ion is equal to the charge of the ion
3. Oxidation numbers of group 1A and 2A elements are always +1 and +2, respectively
4. The oxidation number of hydrogen is +1 in most hydrogen-containing compounds
5. The oxidation number of oxygen is -2 in most oxygen-containing compounds
6. In binary molecular compounds, the more electronegative element is assigned a negative oxidation number, equal to its charge in binary ionic compounds
    - In binary ionic compounds, the oxidation number of halogens (F, Cl, Br) is -1.
7. For a compound, the sum of the oxidation numbers is equal to zero; for a polyatomic ion, the sum of the oxidation numbers is equal to the charge of the polyatomic ion

Try these:

S in H_2S Fe in Fe^{3+} N in HNO_3 Cl in ClO_3^- Oxygen in O_2

Redox and non-redox chemical reactions

- To determine whether a reaction is redox or not, you need to check the oxidation numbers of the elements involved. If the oxidation number of any element changes in going from reactants-to-products, the reaction is a redox reaction

- E.g.,

$$\underset{\underset{\textcircled{+2}}{\uparrow}}{\mathrm{Fe}}\underset{\underset{-2}{\uparrow}}{\mathrm{O}} + \underset{\underset{\textcircled{+2}}{\uparrow}}{\mathrm{C}}\underset{\underset{-2}{\uparrow}}{\mathrm{O}} \rightarrow \underset{\underset{\textcircled{0}}{\uparrow}}{\mathrm{Fe}} + \underset{\underset{\textcircled{+4}}{\uparrow}}{\mathrm{C}}\underset{\underset{-2}{\uparrow}}{\mathrm{O_2}}$$

Fe is reduced

C is oxidized

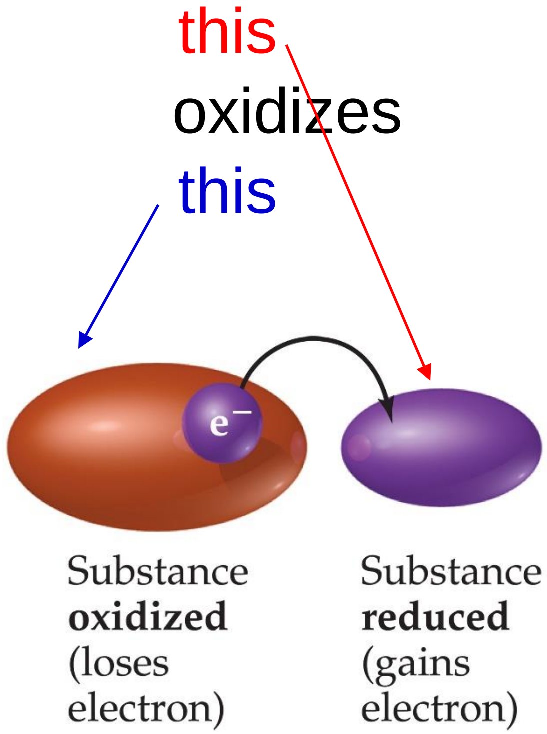
Redox and non-redox chemical reactions

- If the oxidation numbers don’t change, the reaction isn’t redox (would be called non-redox)

$$\underset{+2}{\mathrm{Ca}}\,\underset{+4}{\mathrm{C}}\,\underset{-2}{\mathrm{O}_3} \rightarrow \underset{+2}{\mathrm{Ca}}\,\underset{-2}{\mathrm{O}} + \underset{+4}{\mathrm{C}}\,\underset{-2}{\mathrm{O}_2}$$

Terminology associated with redox processes

- When a redox reaction occurs, one reactant loses electrons to a second reactant.
- We can say that the first reactant becomes oxidized and the second reactant becomes reduced.
- Another way of looking at this is that the reactant that is reduced has taken electrons from the reactant that has been oxidized
- The reactant that takes electrons is enabling the oxidation of the other one. We can call this reactant the oxidizing agent.
- Could also say that the reactant that gets oxidized is enabling the reduction of the second reactant, and thus it is sometimes called the reducing agent.



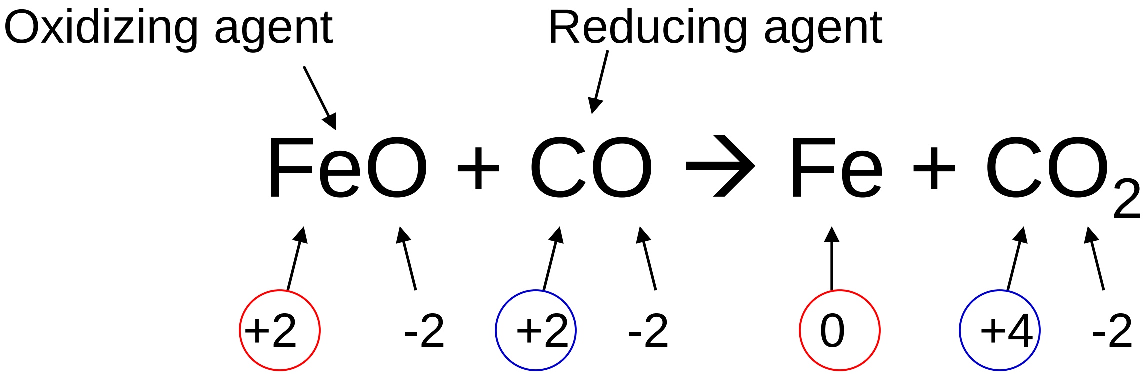
this

oxidizes

this

Terminology associated with redox processes

- Example:



Oxidizing agent

Reducing agent

$$FeO + CO \rightarrow Fe + CO_2$$

+2 -2 +2 -2 0 +4 -2

Since iron (in FeO) gets reduced, FeO is the oxidizing agent (it took electrons from carbon in CO.

Since carbon in CO gets oxidized, CO is the reducing agent (it gave electrons to iron in FeO

Collision theory and chemical reactions

- What causes chemical reactions to take place? There are three requirements that must be met for a chemical reaction to occur:
  - *Molecular collisions*: reactant particles must interact with one another before a reaction can occur
  - *Activation energy*: molecules must collide with a certain, minimum energy, in order for the reaction to take place
  - *Collision orientation*: in many cases, collisions need to involve specific regions (groups of atoms) for a successful reaction to result

Collision theory and chemical reactions

Molecular collisions

- Collisions must occur in order for two or more chemical species to react with each other (reactants can't react if they are separated from each other).
- The collisions involve a transfer of energy, and this energy can be used to break bonds during reactions.

The greater the frequency of collisions the faster the rate.
and
The more molecules present, the greater the probability of collision and the faster the rate (concentration)

Collision theory and chemical reactions

Activation energy

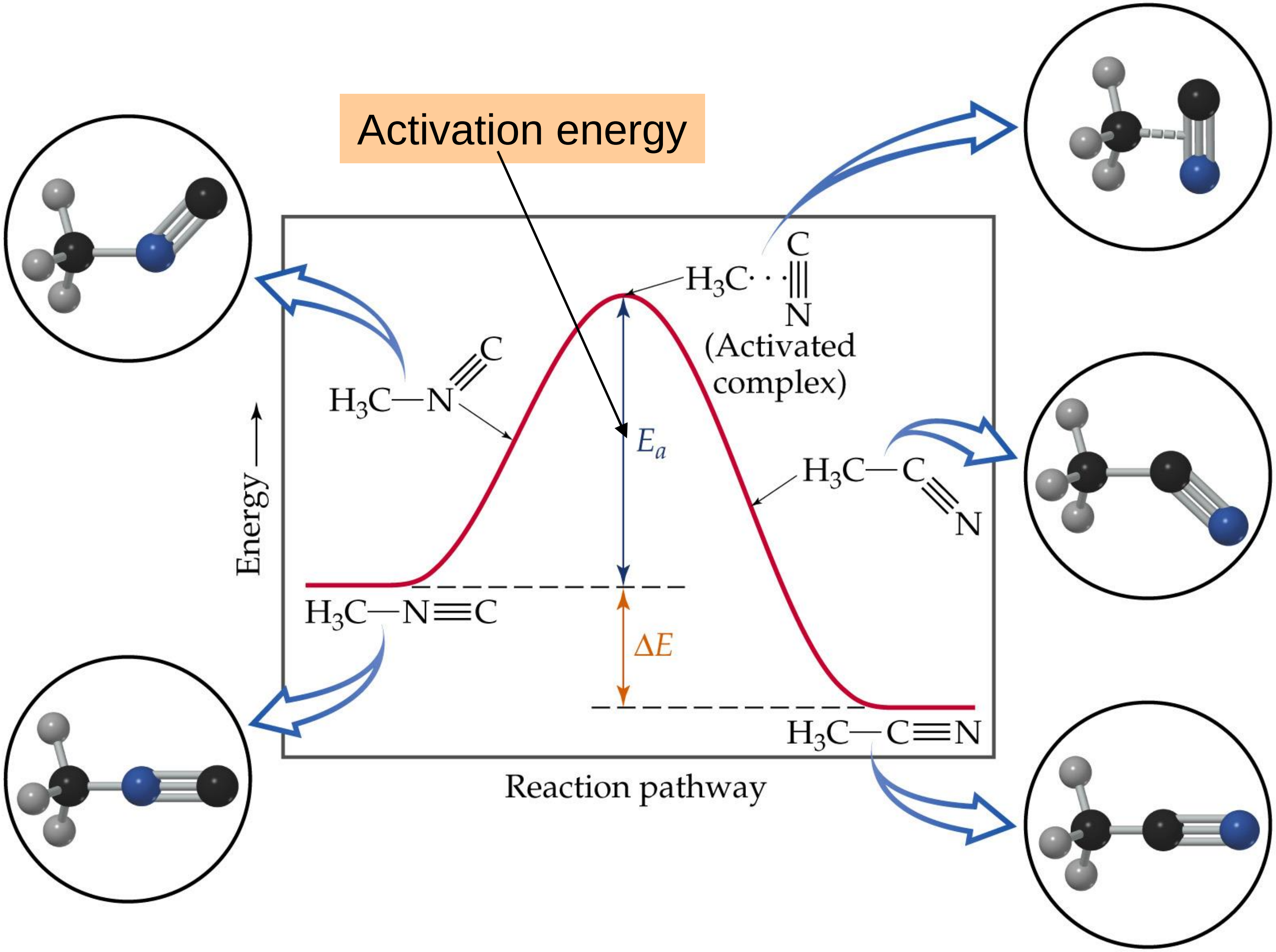
- Activation energy: the energy barrier (kinetic) that must be overcome during the chemical transformation of reactants to products.
- Activation energy varies from reaction to reaction.
- Slow reactions typically have high activation energies (only a small proportion of the molecules in the reaction container have adequate kinetic energy to react).

Higher activation energy barriers yield slower chemical reactions

$CH_3NC \rightarrow CH_3CN$

methyl isonitrile

acetonitrile



Activation energy

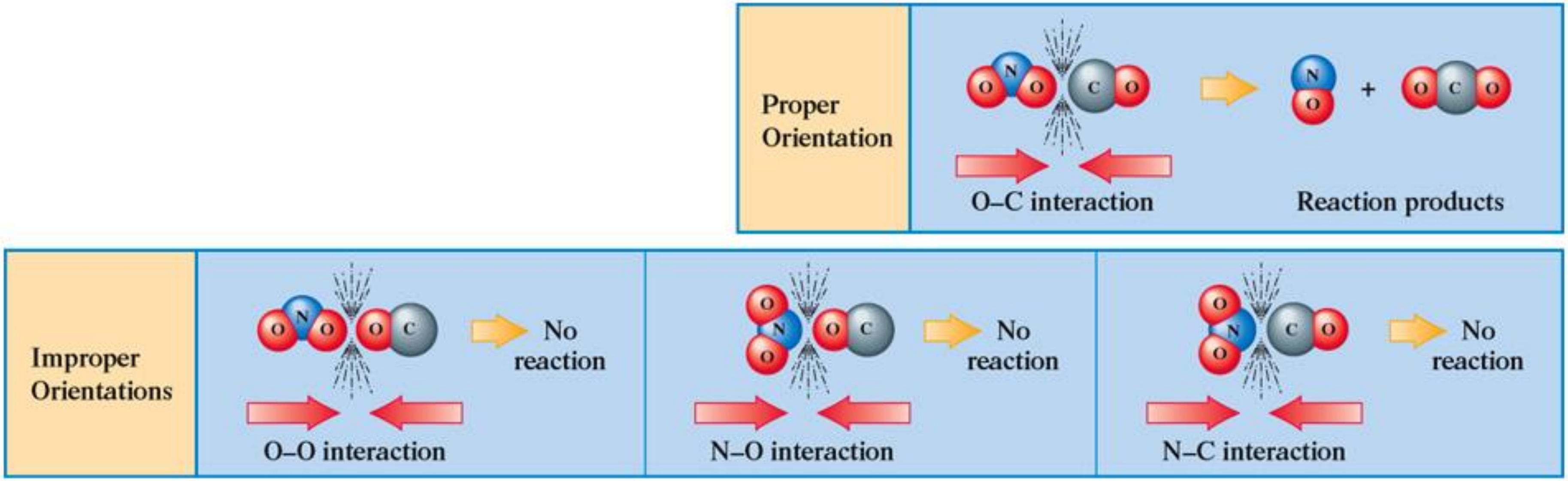
Collision theory and chemical reactions

Collision orientation

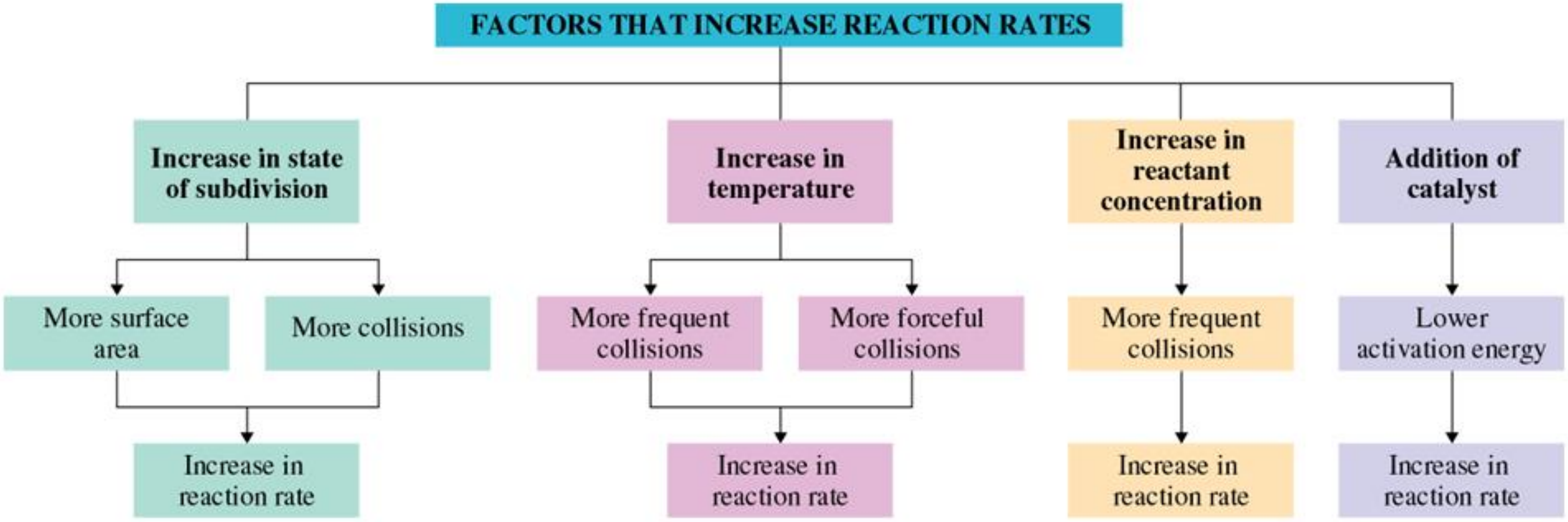
- Bonds are broken and new bonds are formed when reactions occur. New bonds are formed between atoms, and the bonds result from sharing of electrons between those atoms.
- The *atoms that are involved in these new bonds* formed must participate in the collision/contact.

Reactions that have strict orientation requirements tend to be slow

Collision theory and chemical reactions

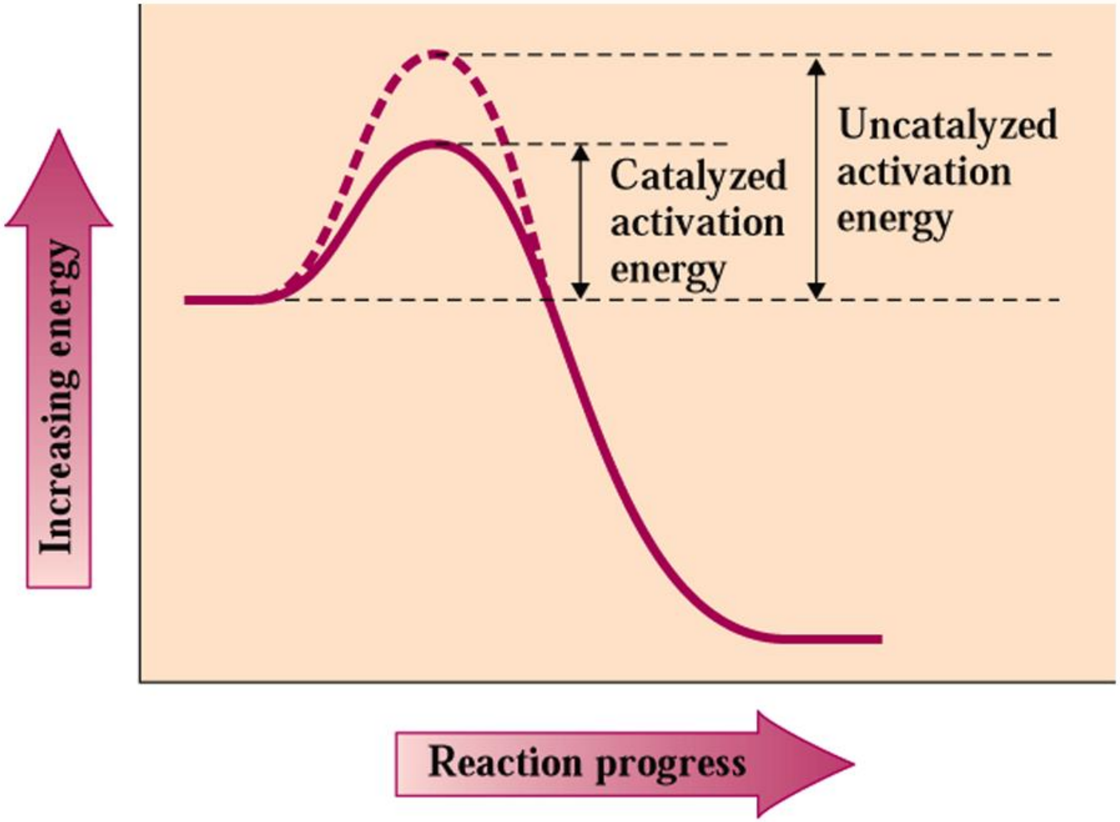


Factors that influence reaction rates



Factors that influence reaction rates

How catalysts affect reaction rates



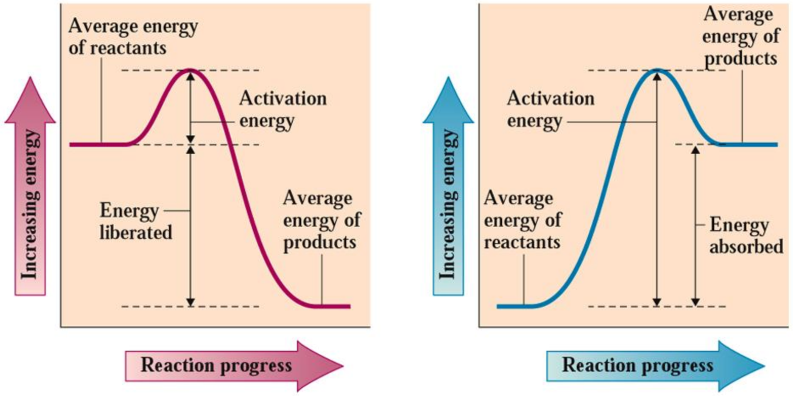
Instead of X + Y → XY

Catalyzed:

1) C + Y → CY
2) X + CY → XY + C

Exothermic and endothermic reactions

- Chemical reactions will produce or consume heat.
- Reactions that consume heat as they occur are called endothermic; reactions that produce heat as they occur are called exothermic



(a) Exothermic reaction

(b) Endothermic reaction

Exothermic and endothermic reactions

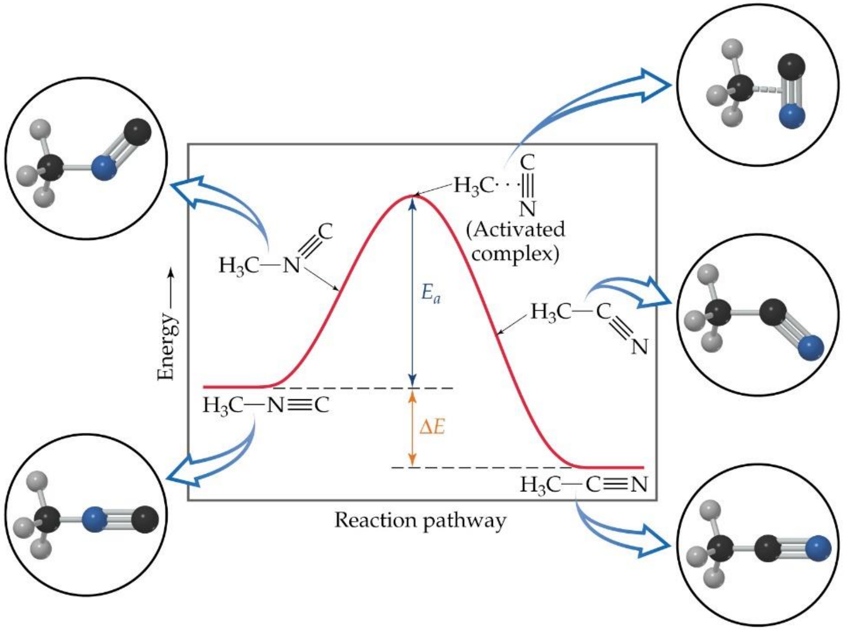
- When chemical reactions occur, bonds must be broken in the reactant molecules and new ones created is the products are formed.
- If the bonds in the reactant molecules are stronger (more stable) than those in the products, the reaction will be endothermic
- If the bonds in the products are more stable than those of the reactants, the reaction will be exothermic

Heat absorbed or released is proportional to

$$\underbrace{[\text{Total energy of bonds broken}]}_{\text{reactants}} – \underbrace{[\text{Total energy of bonds formed}]}_{\text{products}}$$

Chemical equilibrium

- Chemical reactions do not go to “completion” – some of them result in essentially complete consumption of reactants, but even in these cases, there is always at least some small portion of the reactant that remains*
- The reason for this is that reactions can go in both forward and reverse directions



* assuming reaction is carried out in a closed container

Chemical equilibrium

- Consider a chemical reaction like the following one:

$$H_2 + I_2 \rightarrow 2HI$$

- If we start with pure H_2 and I_2, then this reaction is initially fast (*rates are proportional to the concentration of the reactants*) and then begins to slow down as the reactant gets consumed.
- As the reaction occurs, product (HI) begins to build up. The following reaction begins to get faster as the amount of HI builds up:

$$H_2 + I_2 \leftarrow 2HI$$

Chemical equilibrium

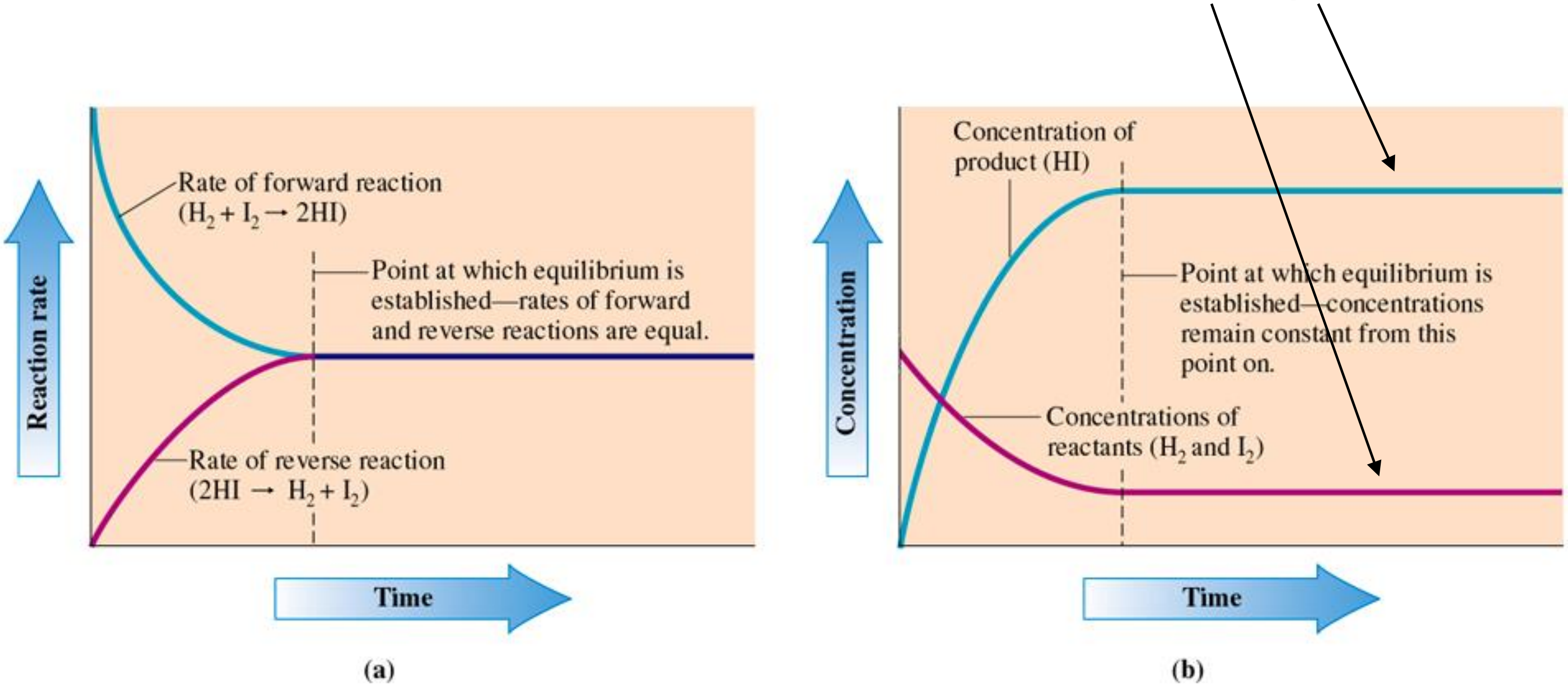
- The two, simultaneous reactions can be described by the following equation:

$$H_2 + I_2 \leftrightarrows 2HI$$

- As the reactions continue, the “forward” reaction (left-to-right) slows down, and the “reverse” reaction (right-to-left) speeds up until their rates become equal.
- At this time (and all times after) the reaction has reached a state of chemical equilibrium (opposed chemical reactions occurring at equal rates)

Chemical equilibrium

Amounts of product and reactant
are constant after equilibrium reached



(a) (b)

Rates

Concentrations

Equilibrium constants

- The amounts of product and reactant that exist once chemical equilibrium is established can be described by a number called an equilibrium constant
- The equilibrium constant is a numerical value that characterizes the relationship between the concentrations of reactants and products *in a system at equilibrium*
- For some general equilibrium reaction:

$$wA + xB \leftrightarrows yC + zD$$

$$K_{eq} = \frac{[C]^y[D]^z}{[A]^w[B]^x}$$

Equilibrium constants

- Equilibrium constant expressions basically indicate the ratio of products to reactants at equilibrium (the concentration of each being raised to the power of its coefficient in the balanced chemical equation)

Square brackets indicate concentration in molarity

$$K_{eq} = \frac{[C]^y[D]^z}{[A]^w[B]^x}$$

coefficients become exponents

$$wA + xB \rightleftarrows yC + zD$$

Only solution species (concentrations) and gases are entered into the equilibrium constant expression. **Solids and pure liquids are not considered.**

Equilibrium constants

- Example, for the reaction

$$2Cl_2(g) + 2H_2O(g) \leftrightarrows 4HCl(g) + O_2(g)$$

The equilibrium constant expression would be written as:

$$K_{eq} = \frac{[HCl]^4[O_2]}{[Cl_2]^2[H_2O]^2}$$

Equilibrium constants

- If concentrations for reactants and products are available, a numerical value for the equilibrium constant can be determined.
- Example: for $N_{2(g)} + 3H_{2(g)} \leftrightarrows 2NH_{3(g)}$, the following concentrations were determined at equilibrium:

N_2: 0.079 M
H_2: 0.12M
NH_3: 0.0051 M

$$K_{eq} = \frac{[NH_3]^2}{[N_2][H_2]^3}$$

$$K_{eq} = \frac{[0.0051]^2}{[0.079][0.12]^3}$$

$$K_{eq} = 0.19$$

Equilibrium constants

- Another example: write an expression for K_{eq} for the following reaction, and calculate K_{eq} if the following concentrations are present at equilbrium:

$$AgCl_{(s)} \leftrightarrows Ag^{+}_{(aq)} + Cl^{-}_{(aq)}$$

At equilibrium

$Ag^{+}_{(aq)} = 1.3 \times 10^{-5}$ M

$Cl^{-}_{(aq)} = 1.3 \times 10^{-5}$ M

Equilibrium constants

Value of K_{eq}	**Relative Amounts of Products and Reactants**	**Description of Equilibrium Position**
very large (10^{30})	essentially all products	far to the right
large (10^{10})	more products than reactants	to the right
near unity (between 10^3 and 10^{-3})	significant amounts of both reactants and products	neither to the right nor to the left
small (10^{-10})	more reactants than products	to the left
very small (10^{-30})	essentially all reactants	far to the left

The size of K_{eq} (size of the number) gives a picture of what the reaction has produced (and what reactants are left) once equilibrium has been reached

Altering equilibrium conditions: Le Chatelier’s principle

- Chemical equilibrium is a balancing act that exists under a certain set of conditions. If the conditions are changed, equilibrium can be upset
- When this occurs, the chemical reaction responds in a way that takes it back to equilibrium (though the final “picture” will probably look a little different than what it looked like before equilibrium was upset)

Altering equilibrium conditions: Le Chatelier’s principle

- Consider the following reaction:

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

- If this reaction has reached equilibrium, what happens if we add some more $H_{2(g)}$?

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

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

The concentrations of the reactants for this reaction have been increased.

Altering equilibrium conditions: Le Chatelier’s principle

- The reaction will respond in a way that will take it back to equilibrium. It does this by minimizing the stress that has been applied to the system

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

Stress here is too much H_2. Reaction will “shift-to-the-right” to consume the extra H_2

Altering equilibrium conditions: Le Chatelier's principle

$$K_{eq} = \frac{[NH_3]^2}{[N_2][H_2]^3}$$

$$K_{eq} = \frac{[5.0]^2}{[5.0][7.0]^3}$$

$$K_{eq} = 0.015$$

before

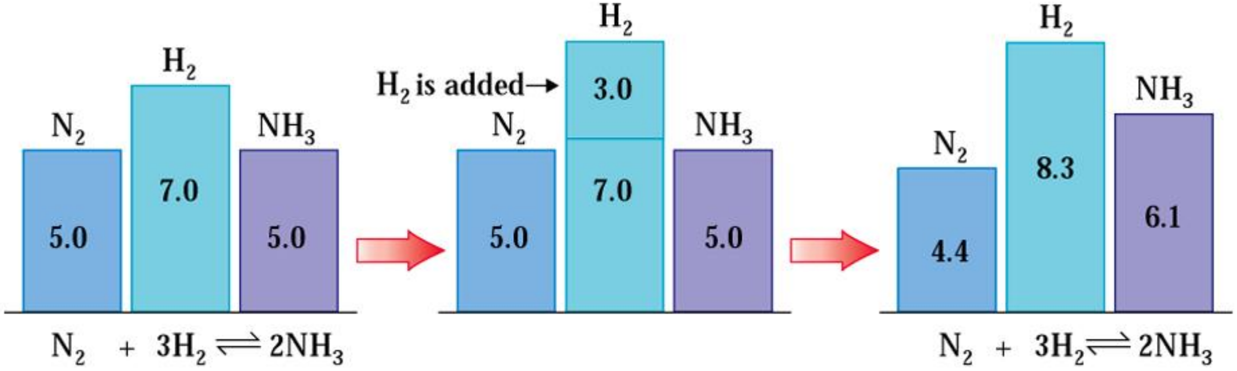
$N_{2(g)} + 3H_{2(g)} \leftrightarrows 2NH_{3(g)}$

$$K_{eq} = \frac{[NH_3]^2}{[N_2][H_2]^3}$$

$$K_{eq} = \frac{[6.1]^2}{[4.4][8.3]^3}$$

$$K_{eq} = 0.015$$

after



(a) Original equilibrium conditions

(b) Increase in $[H_2]$ upsets equilibrium; reaction shifts to the right as more N_2 reacts with the additional H_2.

(c) New equilibrium conditions. Compared with the original equilibrium in (a):

$[N_2]$ has decreased.

$[H_2]$ has increased because of addition. (Note that $[H_2]$ is actually decreased from conditions at (b) because some of it has reacted with N_2 to form more NH_3).

$[NH_3]$ has increased.

Altering equilibrium conditions: Le Chatelier’s principle

- Another way that equilibrium can be influenced: removal of product or reactant.

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

If you were to *remove* $NH_{3(g)}$ as it gets formed, you could drive this reaction completely to the right (consume all reactants)

Altering equilibrium conditions: Le Chatelier’s principle

Temperature changes

- Temperature changes can also affect chemical equilibria.
- Exothermic reactions will “shift-to-the-left” when they are heated, and “shift-to-the-right” when they are cooled

$$H_{2(g)} + F_{2(g)} \leftrightarrows 2HF_{(g)} + \text{heat}$$

(an example of an exothermic reaction)

Altering equilibrium conditions: Le Chatelier’s principle

Temperature changes

- Endothermic reactions will “shift-to-the-right” when they are heated, and “shift-to-the-left” when they are cooled

heat + $2CO_{2(g)} \leftrightharpoons 2CO_{(g)} + O_{2(g)}$

(an example of an endothermic reaction)

Altering equilibrium conditions: Le Chatelier's principle

- For reactions involving gaseous reactants or products, the pressure exerted on the reaction may influence the position of an equilibrium

$$2H_{2(g)} + O_{2(g)} \leftrightarrows 2H_2O_{(g)}$$

Important: for pressure to have an influence, the following must be true:

-there must be unequal numbers of product and reactant gas molecules in the balanced equation

-a pressure change must be brought about by a volume change, not by the addition of some other, unreactive gas that is not involved in the balanced equation

Altering equilibrium conditions: Le Chatelier’s principle

- Example: how will the gas-phase equilibrium shown below react to the following changes:

$$CO_{(g)} + 3H_{2(g)} \leftrightarrows CH_{4(g)} + H_2O_{(g)} + \text{heat}$$

1. Removal of CH_4(g)
2. Addition of H_2O(g)
3. Decrease in the temperature
4. Decrease in the volume of the container