11
Chemical Kinetics

Objective

When you have completed study of this chapter you should be able to:

- Explain the classification of chemical reactions;
- Understand the significance of reactors ;
- Know the importance of catalyst in process reactions.

11.1 Chemical Reactions – Basic Concepts

A chemical reaction is a process in which material changes from a beginning mass to a resulting substance. The significance of a chemical reaction is that new material or materials are produces along with the disappearance of the mass that changed to make the new. This does not mean that new elements have been made. In order to make new elements, the nuclear contents must change. There are magnitudes of difference in the amounts of energy in ordinary chemical reactions compared to nuclear reactions, the rearrangement of the nuclei of atoms to change to new elements is enormous compared to the smaller energies of chemical changes. A chemical equation is a best method to describe what goes on in a chemical reaction..

Examples of Chemical Changes

Chemical reactions, also called chemical changes, are not limited to happening in a chemistry lab. Here are some examples of chemical reactions with the corresponding chemical equations:

An iron bar rusts. The iron reacts with oxygen in the air to make rust.

4 Fe + 3 O2 $\longrightarrow$ 2 Fe2O3

Methane burns. Methane combines with oxygen in the air to make carbon dioxide and water vapor.

CH4 + 2 O2 $\longrightarrow$ CO2 + 2 H2O

As a general rule, biochemical process make poor examples of basic chemical reactions because the actual reaction is carried on within living things and under enzyme control.

Examples of Physical Changes

Here are some examples of changes that are not chemical reactions. In each case, the original material or materials may be reclaimed by physical processes.

- Water boils out of a kettle or condenses on a cold glass.
- An aluminum pot is put on a burner and gets hot.

- Dry ice goes from a solid to a gaseous form of carbon dioxide (sublimation).
- Gold melts or solidifies.
- Sand is mixed in with salt.
- A piece of chalk is ground to dust.
- Glass breaks.
- An iron rod gets magnetized.
- A lump of sugar dissolves in water.

11.2 Classification of Chemical Reactions

Chemists have identified millions of different compounds and an equal number of chemical reactions to form them. When scientists are confronted with an overwhelming number of things, they tend to classify them into groups, in order to make them easier to study and understand. One popular classification scheme for chemical reactions breaks them up into five major categories or types.

1. Synthesis (also called Direct Combination)

A synthesis reaction involves two or more substances combining to make a more complex substance. The reactants may be elements or compounds, and the product will always be a compound. The general formula for this type of reaction can be shown as;

A + B ---> AB

or

element or compound + element or compound --> compound

Some examples of synthesis reactions are shown below;

$2H_{2(g)} + O_{2(g)} \text{---->} 2H_2O_{(g)}$

$C_{(s)} + O_{2(g)} \text{---->} CO_{2(g)}$

$CaO_{(s)} + H_2O_{(l)} \text{---->} Ca(OH)_{2(s)}$

2. Decomposition (also called Analysis)

In a decomposition reaction, one substance is broken down into two or more, simpler substances. This type of reaction is the opposite of a synthesis reaction, as shown by the general formula below;

AB ----> A + B

or

Compound ---> element or compound + element or compound

Some examples of decomposition reactions are shown below;

$C_{12}H_{22}O_{11(s)}$ ----> $12C_{(s)} + 11H_2O_{(g)}$

$Pb(OH)_{2(cr)}$ ----> $PbO_{(cr)} + H_2O_{(g)}$

$2Ag_2O_{(cr)}$ ----> $4Ag_{(cr)} + O_{2(g)}$

3. Single Displacement (also called Single Replacement)

In this type of reaction, a neutral element becomes an ion as it replaces another ion in a compound. The general form of this equation can be written as;

In the case of a positive ion being replaced:

A + BC ----> B + AC
or

In the case of a negative ion being replaced:

A + BC ----> C + BA

in either case we have;

element + compound ----> element + compound

Some examples of single displacement reactions are shown below:

$Zn_{(s)} + H_2SO_{4(aq)}$ ----> $ZnSO_{4(aq)} + H_{2(g)}$

$2Al_{(s)} + 3CuCl_{2(aq)}$ ---> $2AlCl_3(aq) + 3Cu_{(s)}$

$Cl_{2(g)} + KBr(aq)$ ----> $KCl_{(aq)} + Br_{2(l)}$

4. Double Displacement (also called Double Replacement)

Like dancing couples, the compounds in this type of reaction exchange partners. The basic form for this type of reaction is shown below;

AB + CD ----> CB + AD
or
Compound + Compound ----> Compound + Compound

Some examples of double displacement reactions are shown below;

$AgNO_{3(aq)} + NaCl_{(aq)}$ ----> $AgCl_{(s)} + NaNO_{3(aq)}$

$ZnBr_{2(aq)} + 2AgNO_{3(aq)}$ ----> $Zn(NO_3)_{2(aq)} + 2AgBr_{(cr)}$

$H_2SO_{4(aq)} + 2NaOH_{(aq)}$ ----> $Na_2SO_{4(aq)} + 2H_2O_{(l)}$

5. Combustion

When organic compounds like propane are burned, they react with the oxygen in the air to form carbon dioxide and water. The reason why these combustion reactions will stop when all available oxygen is used up is because oxygen is one of the reactants. The basic form of the combustion reaction is shown below;

hydrocarbon + oxygen ----> carbon dioxide and water

Some examples of combustion reactions are;

$CH_{4(g)} + 2O_{2(g)}$ ----> $2H_2O_{(g)} + CO_{2(g)}$

$2C_2H_{6(g)} + 7O_{2(g)}$ ----> $6H_20_{(g)} + 4CO_{2(g)}$

$C_3H_{8(g)} + 5O_{2(g)}$ ----> $4H_2O_{(g)} + 3CO_{2(g)}$

11.3 Chemical Process Reactors

When the reaction proceeds the reactants decrease in concentration while the products increase in concentration. Consider the following two reactions:

A + B --> C

A + C --> D

where C is the desired product. Let's assume that this reaction takes place over a solid catalyst.

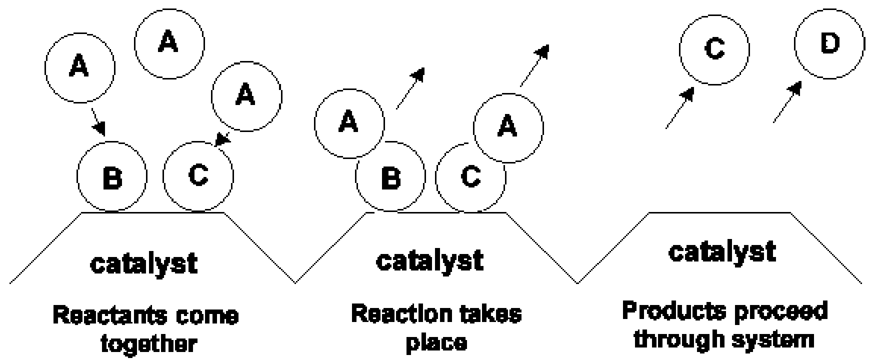

Figure 11.1
Schematic Representation of a Reaction Process

The reaction concentration profile may resemble:

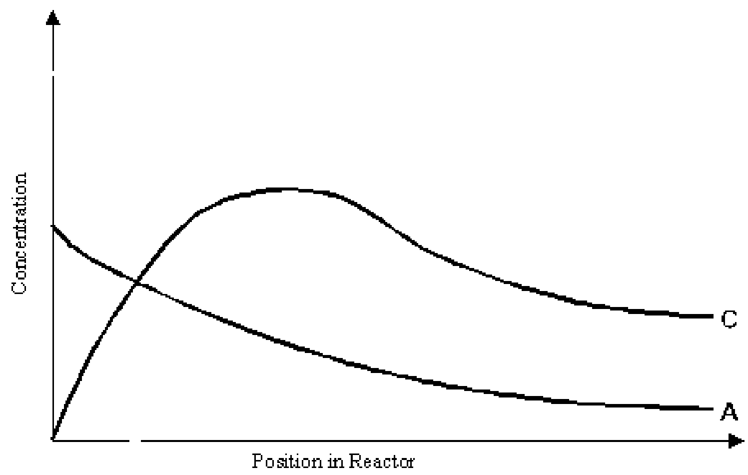

Figure 11.2
A Typical Reaction Profile

11.3.1 Classification Of Reactors

In general, chemical reactors have been broadly classified in two ways, one according to the type of operation and the other according to design features. The former classification is mainly for homogeneous reactions and divides the reactors into batch, continuous, or semi-continuous types. A brief description of these types are as follows.

Batch Reactor

This type takes in all the reactants at the beginning and processes them according to predetermined course of reaction during which no material is fed into or removed from the reactor. Usually it is in a form of tank with or without agitation and is used primarily in a small-scale production. Most of the basic kinetic data for reactor design are obtained from the type.

Continuous Reactor

Reactants are introduced and products withdrawn simultaneously in a continuous manner in this type of reactor. It may assume the shape of a tank, a tubular structure or a tower and finds extensive applications in large-scale plants for the purpose of reducing the operating cost and facilitating control of product quality.

Semi continuous Reactor

The reactors that do not fit either of the preceding two types, belong to this category. In one case, some of the reactants are charged at the beginning, and the remaining are fed continuously as the reaction progresses. Another type is similar to a batch reactor, except that one or more of the products is removed continuously.

11.4 Catalysts

A catalyst is a substance which changes the rate of a chemical reaction (usually speeding it up), but when the reaction is finished, the catalyst is chemically the same as it was at the beginning. This means that none of it is used up in the reaction

Catalysts are quite substrate-specific, which means that they are only good at changing the rate of one type of chemical reaction and not much good with any others.

Catalysts are very important in industry, where it would be uneconomic (or even impossible) to carry out certain chemical reactions. Examples of industrial processes which use catalysts are:

- Making margarine from vegetable oils (Nickel catalyst).
- Making sulphuric acid (Vanadium catalyst).
- Making ammonia (Iron catalyst).
- Making nitric acid (Platinum catalyst).
- Making sulphur dioxide (Platinum catalyst).
- Making polymers (plastics) (Titanium catalyst).
- All these catalysts are either made from, or contain, transition metals

11.4.1 Classification of Catalyst

Homogeneous Catalyst

A catalyst in the same phase (usually liquid or gas solution) as the reactants and products is called homogeneous catalyst.

Heterogeneous Catalysts

A catalyst that is in a separate phase from the reactants is said to be a heterogeneous, or contact, catalyst. Contact catalysts are materials with the capability of adsorbing molecules of gases or liquids onto their surfaces. An example of heterogeneous catalysis is the use of finely divided platinum to catalyze the reaction of carbon monoxide with oxygen to form carbon dioxide. This reaction is used in catalytic converters mounted in automobiles to eliminate carbon monoxide from the exhaust gases. Because heterogeneous catalysts often are used in high temperatures reactions, they are usually high melting (refractory) materials, or else they can be supported by refractory materials such as alumina.

Promotors

Promoters are not catalysts by themselves but increase the effectiveness of a catalyst. For example, alumina Al_2O_3, is added to finely divided iron to increase the ability of the iron to catalyze the formation of ammonia from a mixture of nitrogen and hydrogen. A poison reduces the effectiveness of a catalyst. For example, lead compounds poison the ability of platinum as a catalyst. Thus, leaded gasoline shall not be used for automobiles equipped with catalytic converters.

Enzymes- The Biological catalysts

When a catalyst is doing its job in a living thing, this kind of catalyst is called an Enzyme.

Many of the reactions in catabolism are favorable . This means that these reactions will occur spontaneously even outside of a living organism. The problem is, they are way too slow to be of any use in a biological system. If cells did not have ways of speeding up catabolism, life would be nearly impossible. Enzymes accelerate almost all biological reactions.

Enzyme structure

Enzymes are proteins, which themselves are polymers of amino acids. They range in size from 1 x 10^4 daltons to 1 x 10^6 daltons with most being in the 10^5 range. Some enzymes have extra molecules associated with them, besides amino acids, that assist in the reaction they carry out. The protein portion of an enzyme is called the apoenzyme. A cofactor is the non-protein part of an enzyme. Cofacors can be loosely bound, coenzymes or tightly bound, prosthetic groups. The complete enzyme (apoprotein + cofactor) is termed the holoenzyme**.**

Enzyme Function

Enzymes convert a target molecule, the enzymes substrate(s), into a different molecule, the enzymes product(s). Enzymatic reactions can have any number of substrates and products, but for this introduction, lets consider a simple case; an enzyme that has two substrates and one product that are joined together.

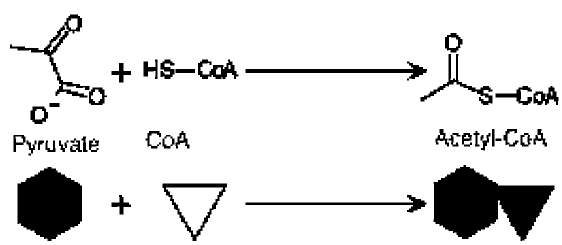

Figure 11.3
An Enzymatic Reaction With Two Substrates and One Product

Enzymes are efficient and specific

The efficiency of enzymes is extremely high. They can catalyze the transformation of as many as 10^2 to 10^6 molecules per minute. Most also have a high degree of specificity binding a specific molecule and converting it to a specific product. Enzyme and substrate fit into each other like a lock into a key.

Visualizing enzymatic catalysis

Many chemical reactions require an initial amount of energy be added to get them to proceed forward. Even thermodynamically favorable reactions need a little boost of energy. It is helpful to imagine a chemical reaction as a roller coaster ride. The activation energy represents the amount of work that goes into having the substrates come together in a manner that causes the reaction to occur.

Enzymes increase the rate of reaction by lowering the activation energy. They lower this activation energy by binding the substrates of the reaction. This causes a reaction to occur for two reasons.

- Enzymes bind their substrates at what is called the active site. When bound at the active site the substrates are brought into close proximity to one another and will react.
- The enzyme will bend the substrates in such a manner to make them more reactive. In biochemistry terminology the enzyme binds the substrates in a transition state complex. This makes it possible for substrates to react and form products.

Most enzymes greatly lower the activation energy of their reaction and allow much more substrate to be converted to product per unit time. Every reaction that we will talk about in metabolism is catalyzed by an enzyme, their importance cannot be overstated.

It is becoming clear that bacteria **are not** little bags of enzymes, but are highly organized. This is reflected in enzyme location. Enzymes are organized by the cell into collections that carry out multi-step conversions. Each enzyme in the collection will take its substrate, convert it to product and hand it off to the next enzyme - analogous to an assembly line. These collections are called biochemical pathways and each is responsible for taking a substrate and converting it into a needed product. Biochemical pathways are classified by their use to the cell and in the next section we will look at different types of catabolic pathways.

The use of enzymes (biological catalysts) in the baking, brewing and dairy industries.

Beverages

Beer and lager are alcoholic drinks made in the following way:

- A source of sugar (barley) is added to water and allowed to grow (barley is a plant!). Enzymes in the mixture start to make sugars.
- The mixture is then flavoured with hops.
- After a bit of a technical process, this mixture has a yeast (a living fungus and there are lots of them) added to it.
- The yeast 'eats' the sugar and gives out alcohol as a waste product.
- When enzymes normally break down sugar (getting energy from the sugar), the following chemical reaction can happen (lots of oxygen is around, so it is called aerobic respiration):

$$C_6H_{12}O_6 \quad + \quad 6O_2 \longrightarrow 6CO_2 \quad + \quad 6H_2O$$

But, in the clean, sterile and almost closed container that beer-making happens, there is no oxygen, so a different chemical reaction happens (no oxygen is around, so it is anaerobic respiration):

$$C_6H_{12}O_6 \longrightarrow 2CO_2 + 2C_2H_5OH$$

This is where the alcohol (C_2H_5OH; it is actually called ethanol) comes from. This overall reaction is called Fermentation. Remember, in both reactions, the enzymes are getting energy from the reaction to help the living thing grow, and it is the enzymes which make this happen quickly enough.

Baking

Bread is a food made in the following way:

Flour, water, salt, yeast and other ingredients (to give flavour) are mixed together to give 'dough'. The dough is left to 'rise'. Both of the reactions described above start to happen. The carbon dioxide gas bubbles get trapped in the dough and it starts to get a bit bigger (a bit like a balloon). Alcohol is also made in the dough.The dough is then 'kneaded' to get rid of any big gaps. It may be allowed to rise again, followed by kneading again. The dough is shaped and 'baked' at over 100°C. During the baking, the yeast is killed (remember, it starts as a living fungus), the alcohol evaporates away (no getting drunk on bread then!) and sugars remain, giving extra flavour to the bread once it has cooled.

Fermentation is happening from when the flour and yeast meet, right up to the temperature at which the yeast dies (about 46°C).

When milk 'goes off', this means certain bacteria from around the milk start to multiply using the milk as a food. The waste materials given out by the bacteria are often nasty and, what's more, if we drink the milk, the bacteria may multiply in us! Even some harmless bacteria will 'sour' milk.

Yoghurt:

Milk contains sugar. The bacterium Lactobacillus bulgaricus is added to the milk and its enzymes ferment the sugar (at about 43°C for 4 to 5 hours) into lactic acid. It is this acid the gives yoghurt its pleasant acidic taste! It is also this acid which stop harmful bacteria from multiplying. The yoghurt is now more like a watery paste.

Fruit and their juices can be added to give a range of flavoured yoghurts.

Most yoghurts we buy have been pasteurised (heated to the kill the bacteria), but this is not done to 'live' yoghurts which still have the bacteria doing their job .

Another microbe called Streptococcus thermophilus is also present in live yoghurt giving it its creamy flavour. Some yeasts may also be present.

Cheese

Traditionally, an enzyme called rennin was taken form the stomach juices of calves. When this enzyme is added to milk, it starts to 'clot' (form a paste). If the watery part of the mixture (the 'whey') is removed, the part which is left behind is the 'curd', the raw material of cheese. Salt is then added.

Because some people have a problem using enzymes from animals, some specially-designed Lactobacillus bacteria are used instead to make the curd.

There are many cheeses. The curd can be allowed to age slightly to give cream cheeses or it can be squeezed and left much longer to slightly decompose giving Cheddar and Cheshire cheeses. If the curd is left long enough, decomposition goes so far that the cheese starts to turn back into a liquid giving

Enzyme-catalysed reactions & temperature

One of the things about enzymes is that, although they are great at speeding up some reactions, they are usually quite fragile when it comes to high temperatures. They are also not too good at working at low temperatures. This is why our bodies need to stay at the important internal temperature of 37°C, so that enzymes can work well.

Some clothes washing powders contain enzymes. They are called 'Biological' or 'Bio' washing powders.

The enzymes are useful because they will clean clothes at quite low emperatures, protecting the fabric from heat damage.

- When food decomposes, the bacteria which are doing this are using their enzymes to make the food 'go off'. If we cool the food down to low temperatures, the enzymes are no way near as good at their jobs and so the food lasts longer. This is one reason why we keep many foods in the refrigerator and freezer.
- If the bacteria make the food 'go off', then if the enzymes working, then the food will last longer. This is one reason why we cook food.

11.4.2 Chemical Absorptions

Solid defects ,in solid surfaces are two-dimensional defects. They offer a potential for attraction to molecules of gases and liquid. Adsorption takes place as molecules are attracted to the surface, and when molecules penetrate through the bulk material, the term absorption is used. Absorption with no chemical bonds formed or broken is called physical absorption or physisorption, whereas chemisorptions refer to processes when new bonds are formed or broken.

If the absorbed species are very stable, and much energies are release in the chemisorption process, the absorbed species are not reactive. Their absorbtions prevent further absorption of other species, making the catalyst inactive. These phenomena are known as catalyst poisoning.

A poison reduces the effectiveness of a catalyst. Tetraethyl lead has been additive to the gasoline. For environmental protection, catalytic converters have been installed in automobiles to oxidize carbon monoxide and hydrocarbons. However, lead compounds poison the ability of platinum as a catalyst. Thus, leaded gasoline should not be used for automobiles equipped with catalytic converters.

There are many types of catalyst in the market place, for example MIRATECH oxidation catalyst can also reduce carbon monoxide and hydrocarbon emissions. The most common catalytic converter uses Pt metal.

Recently, there is a concern over the reduction of sulfur in gasoline and other engine fuels for the purpose of reducing sulfur oxides emission. Technically, sulphur compounds are not catalyst poisons (i.e. they do not cause an irreversible reduction in catalyst efficiency). However, they will occupy part of the precious metal surface, thereby reducing the active conversion of exhaust emissions until the sulphur gets de-sorbed from the precious metal sites again (short-term effect).

114.3 Transition Metals As Catalysts

The first period of transition metals are represented by these metals.

Sc Ti V Cr Mn Fe Co Ni Cu and Zn

Typical common features among them are the presences of *d* electrons, and in many of them, and their unfilled *d* orbitals. As a result, transition metals form compounds of variable oxidation states. Thus, these metals are *electron banks* that lend out electrons at appropriate time, and store them for chemical species at other times.

11.4.4 Metal Clusters

The surface area per unit weight is an important consideration when solids are utilized as catalysts. There are numerous studies related to the study of surface area of particulate metals. Various methods are developed to measure the surface areas of solid materials. One such method is the surfact area determination from gas adsorption.

Clusters are the limiting sizes of metal particles, each of which are made up only a few atoms. There is no need to rigorously define the number of atoms in a particulate to be called clusters, but a general view is that when the number of atoms at the surface of the particle is more than the nuber of atoms in the interior, the particle is a cluster. Thus, a cluster can have as few as 3 atoms, and as large as a few tens of atoms.

11.4.5 Photocatalytic Reactions

Reactions which are caused by photons, bundles of radiation energy, are called photolysis. Photocatalyic reactions imply photolysis in the presence of a catalyst. In most cases, however, the catalysts are semiconductors and the reactions are semiconductor assisted photolysis reactions. In this regard, the photocatalyst has a slightly different function than those in thermal chemical process.