

What Is Runaway Polymerization?

A runaway polymerization is a potentially dangerous reaction in which chemical products form with excessive speed, producing heat that may lead to an explosion or other hazards. Because polymerization is an essential process for making many synthetic materials, chemists adopt strategies to maintain safe reactions and avoid runaway polymerization.

Monomers and Polymers

Most plastics and many biological molecules belong to a class of chemical compounds called polymers -- long chains of the same chemical units repeated continually. Each unit in the chain is a molecule called a monomer. For example, polystyrene is a polymer consisting of many styrene molecules linked together. In this case, styrene is the monomer.

Polymerization

To [make plastics](#), a chemical process takes a container of a monomer substance and combines it with other chemicals which initiate the polymerization process. During the reaction, the monomers, which are normally stable on their own, link together. The monomer molecules stick together in repeating chains, forming polymers, and continues until the container runs out of initiator chemicals or available monomers. The resulting polymer gains properties, such as strength and elasticity, lacking in the original monomer.

Runaway Polymerization

Some polymerization reactions are exothermic -- meaning they give off heat. Ideally, the total heat produced is small and dissipates harmlessly into the reaction container. However, if a large amount of monomer is involved, and if the reaction is strongly exothermic, the monomers may combine too quickly. As a consequence, excessive heat and pressure build up in the reaction vessel, melting the equipment or causing an explosion.

Preventative Measures

Chemical engineers use a variety of methods to prevent runaway polymerization. The equipment may incorporate stirring devices that help break up areas where reaction speed is too great and dissipate heat through the mixture. A chemist may add compounds, called inhibitors, to deliberately slow the reaction, keeping the rate below the point at which it runs away. They also add emergency devices that open automatically if the reaction pressure exceeds a safe value. These components prevent the reaction vessel from exploding with violent force.

What Is Gibbs Free Energy?

Most likely, the first chemical reactions you studied in school moved in one direction; for example, vinegar poured into baking soda to make a "volcano." In reality, most reactions should be illustrated with an arrow pointing in each direction, meaning the reaction could go both ways. Ascertaining the Gibbs free energy of a system offers a way to determine whether one arrow is much larger than the other; i.e., does the reaction almost always go in one direction, or are they are both close to the same size? In the latter case, the reaction is just as likely to go one way as the other. The three critical factors in calculating the Gibbs free energy are enthalpy, entropy, and temperature.

Enthalpy

Enthalpy is a measure of how much energy is contained in a system. A primary component of enthalpy is internal energy, or the energy from the random movement of molecules. Enthalpy is neither the potential energy of molecular bonds nor the kinetic energy of a moving system. The molecules in a solid move much less than those of a gas, so the solid has less enthalpy. The other factors in calculating enthalpy are the pressure and volume of the system, which are most important in a gas system. Enthalpy is changed when you do work on a system, or if you add or subtract heat and/or matter.

Entropy

You can think of entropy as a measure of the thermal energy of a system or as a measure of the disorder of the system. To see how the two are related, think about a glass of water that freezes. When you take heat energy away from the water, the molecules that were moving freely and randomly become locked in a solid and very ordered ice crystal. In this case, the change in entropy for the system was negative; it became less disordered. At the level of the universe, entropy is always increasing.

Relationship to Temperature

Enthalpy and entropy are influenced by temperature. If you add heat to the system you will increase both entropy and enthalpy. Temperature is also included as an independent factor in calculating Gibbs free energy. You calculate the change in the Gibbs free energy by multiplying the temperature by the change in entropy, and subtracting the product from the change in enthalpy for the system. From this, you can see that temperature can dramatically change the Gibbs free energy.

Relevance in Chemical Reactions

Being able to calculate the Gibbs free energy is important because you can use it to determine how likely a reaction is to occur. Negative enthalpy and positive entropy favor a reaction going forward. Positive enthalpy and negative entropy do not favor a reaction going forward; these reactions will go in the reverse direction, regardless of temperature. When one factor favors the reaction and the other does not, temperature determines which direction the reaction will go. If the change in Gibbs free energy is negative, the reaction will go forward; if it is positive, it will go in reverse. When it is zero, the reaction is at equilibrium.

Chemical Vs. Physical Reactions

Reactions between two or more molecules result in physical or chemical changes. Physical changes alter matter's appearance and chemical changes alter matter's composition but definitely, heat changes them both.

Reaction

A reaction happens when two or more molecules, or groups of atoms, interact. The result depends on the type of molecule and how they interact. The interaction causes either a physical or a chemical change.

Physical Change

If a physical change occurs, the matter involved remains the same at its molecular level. The molecules rearrange, but the internal structure stays intact. It may look different but it has the same material.

An example of Physical Change

The change from water to ice shows an example of physical change. Lowering the temperature of the water causes it to freeze and to take on a different shape, but it still contains hydrogen and oxygen.

Chemical Change

A chemical change occurs when a reaction causes a change at a molecular level. During this reaction, bonds between atoms break or new ones form. After the reaction, the matter's chemical composition changes, and a new substance forms.

An example of Chemical Change

Rusting shows an example of a chemical change. Rusting occurs when iron (Fe), interacts with oxygen (O). The resulting rust, or iron oxide, has a different chemical composition from its original components.

What is a Combustion Reaction?

A combustion reaction, sometimes abbreviated RXN, is any reaction in which a combustible material combines with oxygen or is oxidized. The most common combustion reaction is a fire, in which hydrocarbons burn in air to produce carbon dioxide, water vapor, heat, light and often ashes. While other chemical reactions may produce heat, combustion reactions always share specific characteristics that must be present for a reaction to be a true combustion reaction.

How Combustion Takes Place

For a combustion reaction to proceed, combustible materials and oxygen must be present as well as an external energy source to start the combustion. While some material will spontaneously burst into flame when brought together with oxygen gas, most substances need a spark or other source of energy to start burning. Once the combustion reaction starts, the heat generated by the reaction is enough to keep it going.

For example, when you start a wood fire, the hydrocarbons in the wood combine with oxygen in the air to form carbon dioxide and water vapor, releasing energy in the form of heat and light. To start the fire, you need an external energy source such as a match. This energy breaks the existing chemical bonds so that the carbon, hydrogen and oxygen atoms can react.

The combustion reaction releases much more energy than is needed to break the chemical bonds. As a result, the wood continues to burn until the hydrocarbons are used up. Any nonhydrocarbon impurities in the wood are deposited as ashes. Wet wood does not burn well because turning the water in the wet wood to steam uses up energy. If all the energy produced by the combustion reaction is used for vaporizing the water in the wood, none is left to keep the reaction going, and the fire goes out.

Examples of Combustion Reactions

The combustion of methane, the main component of natural gas, is an example of a typical combustion reaction. Stoves and furnaces running on natural gas have a pilot light or spark to provide the external energy necessary for starting the combustion reaction.

The methane has chemical formula CH₄, and it burns with oxygen molecules from the air, chemical formula O₂. When the two gases come into contact, combustion does not start because the molecules are stable. Within a spark or pilot light, the single oxygen bond and the four methane bonds are broken, and the individual atoms react to form new bonds.

Two oxygen atoms react with the carbon atom to form a molecule of carbon dioxide, and two more oxygen atoms react with the four hydrogen atoms to form two molecules of water. The chemical formula is $\text{CH}_4 + 2\text{O}_2 = \text{CO}_2 + 2\text{H}_2\text{O}$. The formation of the new molecules releases a substantial amount of energy in the form of heat and light.

The combustion of magnesium does not release carbon dioxide or water vapor, but it is still a combustion reaction because it is an exothermic reaction of a combustible material with oxygen. Placing magnesium in the air is not enough to start combustion, but a spark or flame breaks the bonds of the oxygen molecules in the air to allow the reaction to proceed.

The magnesium combines with oxygen from the air to form magnesium oxide and excess energy. The chemical formula for the reaction is $\text{O}_2 + 2\text{Mg} = 2\text{MgO}$, and the excess energy is released in the form of intense heat and bright, white light. This example shows that a chemical reaction may be a combustion reaction without having the characteristics of a traditional fire.