

# Effects in reversible exothermic reactions.

## Effect of Temperature on Equilibrium

A temperature change occurs when temperature is increased or decreased by the flow of heat. This shifts chemical equilibria toward the products or reactants, which can be determined by studying the reaction and deciding whether it is endothermic or exothermic.

## Introduction

Le Châtelier's principle states that a change in temperature, pressure, or concentration of reactants in an equilibrated system will stimulate a response that partially off-sets the change to establish a new equilibrium. In the case of changing temperature, adding or removing of heat shifts the equilibrium.

However, reactions invariably involve changes in [enthalpy](#), with energy (typically in the form of heat, but can involve light) either being absorbed or released during the reaction.

Some chemical reactions -- like burning wood or exploding TNT -- release heat to their surroundings. Chemists call these exothermic reactions. Increasing the temperature affects an exothermic reaction in two different ways: by changing the rate of the reaction and by changing the balance between products and reactants at the end of the reaction.

Generally speaking, your reaction will speed up because a higher temperature means more heat and energy in your system. However, in some cases, raising the temperature might shift equilibrium and prevent some of your reaction from occurring

## Reaction Rates

Nearly all reactions go faster as the temperature increases -- exothermic reactions included. The reaction between oxygen in the air and the chemicals in the tip of a match, for example, is so slow at room temperature that nothing seems to happen. When you heat up the tip of the match by striking it against the striker strip on the box, however, the temperature increases and with it the rate of the reaction until it burns with a hot flame. In general, the more you increase the temperature of an exothermic reaction, the faster it will go.

## Equilibrium

Most chemical reactions can go both ways, meaning they can run forward and convert reactants into products or run in reverse and convert products into reactants. As the reaction runs forward, the reactants are gradually depleted while the products start to accumulate, so the forward

reaction slows down while the reverse reaction speeds up. Eventually the rates of the forward and reverse reactions are the same, so although the reaction continues to occur, the amounts of products and reactants do not change. This steady state is called an equilibrium.

### **Le Chatelier's Principle**

The ratio of reactants to products at equilibrium depends on the specific chemical reaction. For something like fire, for example, little if any of the reactant is left at equilibrium, whereas for something like the reaction between nitrogen and hydrogen to make ammonia, a lot of reactants may be left at equilibrium. Le Chatelier's principle basically says that all chemical systems want to get to and stay at equilibrium. If you add reaction products to a chemical system at equilibrium, you can expect that some amount of product will be converted into reactants, while if you add reactants, some amount of reactants will be converted into products so that equilibrium is maintained.

### **Heat and Equilibrium**

For an exothermic reaction, heat is essentially a product of the reaction. In keeping with Le Chatelier's principle, if you increase the temperature you are increasing the amount of products, and so you shift the balance at equilibrium back toward reactants, meaning there will be more reactants left at equilibrium. The higher the temperature goes, the further the balance at equilibrium shifts back toward reactants. A famous example is the reaction between hydrogen and nitrogen to make ammonia. The reaction is so slow at room temperature that nothing happens. If you increase the temperature to speed the reaction up, however, the balance at equilibrium shifts back towards reactants, and very little ammonia is produced.

### **What Happens in Exergonic Chemical Reactions?**

Reactions are classified as exergonic or endergonic by the change in a quantity called "Gibbs free energy." Unlike endergonic reactions, an exergonic reaction can occur spontaneously, without a need to input work. That doesn't mean a reaction will necessarily occur simply because it's exergonic -- the rate at which the reaction occurs could be so slow that it will never happen on a timescale you care about.

### **Gibbs Free Energy**

Gibbs free energy is not called "free energy" because there's no price tag, but because it measures how much non-mechanical work a system can do. If the reactants in a process have higher Gibbs free energy than the products, the process is called exergonic, meaning that it releases energy. Another way to say this is to describe the reaction as thermodynamically spontaneous, meaning you don't have to do work to make the reaction happen.

## **Exothermic vs. Exergonic**

Many, but not all, exergonic reactions are exothermic, which means they release heat. A reaction can actually be exergonic, however, and yet absorb heat, or be endothermic. Consequently, exothermic and exergonic do not necessarily go together. The key difference between them lies in the difference between work versus heat; an exergonic process releases energy through work, whereas an exothermic process releases energy through heat. Moreover, a process may be exergonic at some temperatures but not at others.

## **Entropy vs. Enthalpy**

Nineteenth-century chemists found spontaneous endothermic reactions quite puzzling; they reasoned that a reaction should be spontaneous if it releases heat. What they were missing was the role of entropy, which is a measure of the amount of energy unavailable for work in a system. If we consider the system as well as its surroundings, a process will be exergonic if it causes a net increase in entropy. Releasing heat to the surroundings causes the entropy to increase, but such a reaction can still absorb heat and be exergonic if the entropy of the system increases by an even larger amount.

## **Considerations**

Evaporation -- the process whereby a liquid turns into a gas -- is associated with a very large positive change in entropy. Exergonic reactions that absorb heat are often reactions that release a gas as one of the products. As the temperature increases, these reactions will become more exergonic. An exothermic reaction that releases heat, by contrast, will be more exergonic at lower temperatures than at higher ones. All of these considerations play a role in determining whether a reaction will be spontaneous.

## **Name One Way to Decrease the Rate of Solvation**

The speed of solvation, the act of chemically dissolving one substance by another, depends on what the substances are, and various other factors such as stirring. Because all chemical-reaction rates are tied to temperature, lowering the temperature of a solvation reaction will decrease its rate, all other factors being equal.

## **Solution Reactions**

Solution reactions occur when the molecules of two substances mix, either completely or incompletely. When a substance doesn't dissolve, it remains as a solid lump or a separate layer of liquid next to the solvent, as what happens with oil and water. Generally speaking, the principle, "like dissolves like" applies to solvation; polar molecules, such as water, dissolve others, including alcohol. Non-polar molecules, such as naphthalene, mix well with others, such as benzene.

## **Rate of Solvation and Heat**

Solvation doesn't happen instantly, but at a rate determined by the type and amounts of substances involved, the temperature, and how saturated the solution becomes. As a solution becomes more saturated, the solution reaction slows. For substances that dissolve marginally or slowly, chemists can increase the rate of solvation by heating the solution.

## **Arrhenius Equation**

A formula called the Arrhenius equation mathematically relates the speed of a chemical reaction to temperature. In a nutshell, the relationship is exponential, where a reaction slows very gradually as the temperature drops, but rises quickly when temperature increases. The equation works for a variety of chemical actions including solvation, clearly indicating the role of temperature in the reaction rate.

## **Limits to Cooling for Rate Change**

You can decrease the rate of solvation by cooling the solution, but the technique works only to the point at which the solution freezes; then it stops completely. Cooling is also complicated by the fact that some solvation reactions produce heat and some consume it. If an exothermic reaction is at equilibrium and you cool it to a small degree, you may actually cause the solvation to speed up because the lower temperature allows for the production of more heat.

## **How Temperature Affects the Equilibrium Constant**

Changing the pressure or the concentrations of the things present in the mixture doesn't change the equilibrium constant, although both of these may affect the position of equilibrium. These changes tend to undo the effect of the change you made.

Temperature, on the other hand, does change the equilibrium constant. For an exothermic reaction (ones that release heat), increasing the temperature reduces the value of the equilibrium constant. For endothermic reactions, which absorb heat, increasing the temperature increases the value of the equilibrium constant.

## **What Are Causes of Chemical Reactions?**

Chemical reactions occur when two substances interact to form new compounds or molecules. These processes are ubiquitous in nature and essential to life; NASA's working definition of life, for example, describes it as a "self-sustaining chemical system capable of Darwinian evolution." Several factors determine when and whether a chemical reaction will occur.

### **Collisions**

When two molecules collide with the right orientation and sufficient force, a chemical reaction may result. Not all collisions cause reactions, however; the atoms or molecules must be able to recombine to form new compounds. Helium atoms, for instance, are inert; they will not react with other gases because their outermost electron shell is already full.

Breaking bonds between atoms takes up energy, while forming new bonds releases energy. If a combination of two atoms has lower energy than the individual atoms, the compound these atoms form is stable. We can use thermodynamics to predict whether such a reaction will occur.

### **Entropy**

Entropy is a measure of disorder. The Second Law of Thermodynamics holds that the entropy of a closed system can never decrease. If a reaction increases the total entropy of the system and its surroundings, the reaction will be spontaneous. Reactions that are not spontaneous only occur when coupled with a spontaneous reaction, or as a result of doing work on a system (i.e., by expending energy, which causes an increase in net entropy). Consequently, the total entropy of the universe always increases.

As an example, your body powers reactions that are not spontaneous (e.g., protein synthesis) using reactions that release energy and cause a large increase in total entropy (e.g., glucose metabolism).

Total entropy is difficult to measure, so chemists predict whether reactions will be spontaneous by calculating the [Gibbs free energy](#), which they define as the heat absorbed by a reaction at constant pressure, minus the temperature, multiplied the change in entropy of the system. A negative Gibbs free energy indicates a spontaneous reaction.