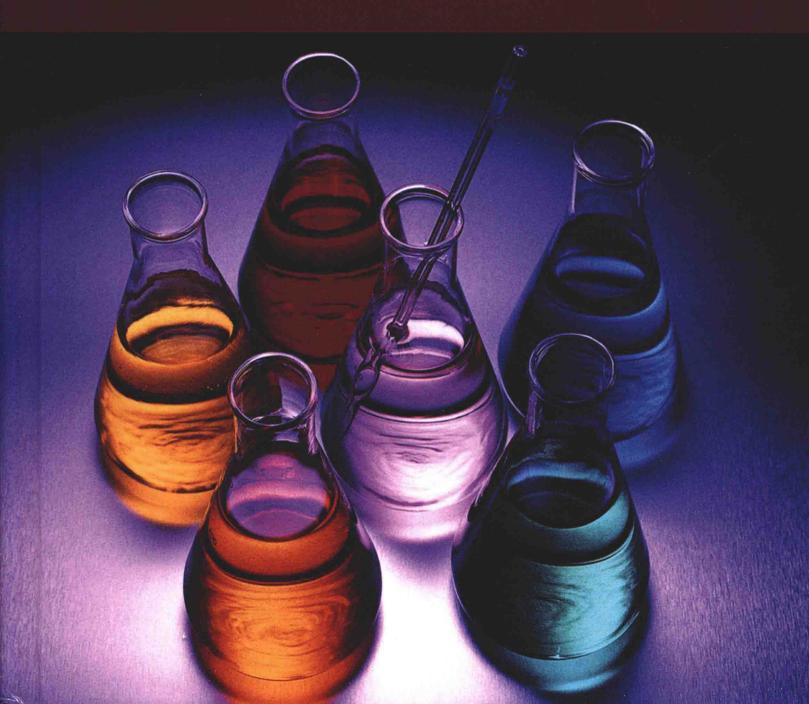
# Principles and Processes of CHEMICAL REACTIONS

Pam Wang, Ph.D.



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**Editor:** 

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## **Principles and Processes of Chemical Reactions**



### About the Editor Pam Wang, Ph.D.

Pam Wang is a chemical biologist by training who has research experience in a variety of interdisciplinary fields. She received her PhD in 2014 studying artificial proteins and is now an industrial postdoc working on bacterial genome engineering. Her interests lie primarily in the application of biophysical, biochemical, and molecular engineering techniques to biotechnology and the pharmaceutical sciences.

### **List of Contributors**

### Marvam Salehi

Department of Medical Biophysics, University of Toronto, Toronto, ON, Canada

### Theodore J. Perkins

Regenerative Medicine Program, Ottawa Hospital Research Institute, Ottawa, ON, Canada

Department of Biochemistry, Microbiology and Immunology, University of Ottawa, Ottawa, ON, Canada

### Masaki Nakagawa

Department of Mathematical and Life Sciences, Graduate School of Science, Hiroshima University, Higashi-Hiroshima, Japan

### Yuichi Togashi

Department of Mathematical and Life Sciences, Graduate School of Science, Hiroshima University, Higashi-Hiroshima, Japan Research Center for the Mathematics on Chromatin Live Dynamics, Hiroshima University, Higashi-Hiroshima, Japan

### Dhiman Maitra

Department of Obstetrics and Gynecology, The C.S. Mott Center for Human Growth and Development, Wayne State University School of Medicine, Detroit, MI, United States of America

### Iyad Ali

Department of Obstetrics and Gynecology, The C.S. Mott Center for Human Growth and Development, Wayne State University School of Medicine, Detroit, MI, United States of America

Department of Biochemistry and Genetics, Faculty of Medicine and Health Sciences, An-Najah National University, Nablus, Palestine

### Rasha M. Abdulridha

Department of Obstetrics and Gynecology, The C.S. Mott Center for Human Growth and Development, Wayne State University School of Medicine, Detroit, MI, United States of America

### Faten Shaeib

Department of Obstetrics and Gynecology, The C.S. Mott Center for Human Growth and Development, Wayne State University School of Medicine, Detroit, MI, United States of America

### Sana N. Khan

Department of Obstetrics and Gynecology, The C.S. Mott Center for Human Growth and Development, Wayne State University School of Medicine, Detroit, MI, United States of America

### Ghassan M. Saed

Department of Obstetrics and Gynecology, The C.S. Mott Center for Human Growth and Development, Wayne State University School of Medicine, Detroit, MI, United States of America

### Subramaniam Pennathur

Division of Nephrology, Department of Internal Medicine, University of Michigan Medical School, Ann Arbor, MI, United States of America

### Husam M. Abu-Soud

Department of Obstetrics and Gynecology, The C.S. Mott Center for Human Growth and Development, Wayne State University School of Medicine, Detroit, MI, United States of America

Department of Biochemistry and Molecular Biology, The C.S. Mott Center for Human Growth and Development, Wayne State University School of Medicine, Detroit, MI, United States of America

### Jakob Fischer

Bio Systems Analysis Group, Institute of Computer Science, Jena Centre for Bioinformatics and Friedrich Schiller University, Jena, Germany Max-Planck-Institute for Biogeochemistry, Jena, Germany

International Max Planck Research School for Global Biogeochemical Cycles, Jena, Germany

### Axel Kleidon

Max-Planck-Institute for Biogeochemistry, Jena, Germany

### Peter Dittrich

Bio Systems Analysis Group, Institute of Computer Science, Jena Centre for Bioinformatics and Friedrich Schiller University, Jena, Germany

### Ian J. Keyte

Division of Environmental Health & Risk Management, School of Geography, Earth & Environmental Sciences, University of Birmingham, Edgbaston, UK

### Roy M. Harrison

Division of Environmental Health & Risk Management, School of Geography, Earth & Environmental Sciences, University of Birmingham, Edgbaston, UK

### Gerhard Lammel

Max Planck Institute for Chemistry, Hahn-Meitner-Weg 1, 55128 Mainz, Germany

Masaryk University, Research Centre for Toxic Compounds in the Environment, Kamenice 5, 62500 Brno, Czech Republic

### **Bart Danon**

Energy Technology, Delft University of Technology, Leeghwaterstraat 44, 2628CA, Delft, The Netherlands

### Gianluca Marcotullio

SEA Servizi Energia Ambiente srl, Via Miraflores 2, 67100, L'Aquila, Italy

### Wiebren de Jong

Energy Technology, Delft University of Technology, Leeghwaterstraat 44, 2628CA, Delft, The Netherlands

### Carsten Hennig

Institute of Physical Chemistry, University of Göttingen, Tammannstr. 6, D-37077 Göttingen, Germany

### Stefan Schmatz

Institute of Physical Chemistry, University of Göttingen, Tammannstr. 6, D-37077 Göttingen, Germany

### Moritz P. Haag

Laboratory of Physical Chemistry, ETH Zurich, Vladimir Prelog route 2, CH-8093 Zurich, Switzerland

### Markus Reiher

Laboratory of Physical Chemistry, ETH Zurich, Vladimir Prelog route 2, CH-8093 Zurich, Switzerland

### **Matthias Peter**

Department of Chemical Physics, Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, 14195 Berlin, Germany

### Sergey Adamovsky

Department of Chemical Physics, Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, 14195 Berlin, Germany

### Jose Manuel Flores Camacho

Department of Chemical Physics, Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, 14195 Berlin, Germany

### Swetlana Schauermann

Department of Chemical Physics, Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, 14195 Berlin, Germany

### Hua Guo

Department of Chemistry and Chemical Biology, University of New Mexico, Albuquerque, New Mexico 87131, USA

### Kopin Liu

Institute of Atomic and Molecular Sciences, Academia Sinica, Taipei 10617, Taiwan

Department of Physics, National Taiwan University, Taipei 10617, Taiwan

### P. Kovaříček

Institute of Science and Supramolecular Engineering, University of Strasbourg, 8 avenue Gaspard Monge, 67000 Strasbourg, France

### A. C. Meister

Institute of Science and Supramolecular Engineering, University of Strasbourg, 8 avenue Gaspard Monge, 67000 Strasbourg, France

### K. Flídrová

Institute of Science and Supramolecular Engineering, University of Strasbourg, 8 avenue Gaspard Monge, 67000 Strasbourg, France

### R. Cabot

Institute of Science and Supramolecular Engineering, University of Strasbourg, 8 avenue Gaspard Monge, 67000 Strasbourg, France

### K. Kovaříčková

Institute of Science and Supramolecular Engineering, University of Strasbourg, 8 avenue Gaspard Monge, 67000 Strasbourg, France

### J.-M. Lehn

Institute of Science and Supramolecular Engineering, University of Strasbourg, 8 avenue Gaspard Monge, 67000 Strasbourg, France

### Martin E. Maier

Institute of Organic Chemistry, University of Tübingen, Auf der Morgenstelle 18, 72076 Tübingen, Germany

### Matthew T. Clough

Department of Chemistry, Imperial College London, London, SW7 2AZ, UK

### Karolin Gever

BASF SE, Ludwigshafen, Germany

### Patricia A. Hunt

Department of Chemistry, Imperial College London, London, SW7 2AZ, UK

### Jürgen Mertes

BASF SE, Ludwigshafen, Germany

### Tom Welton

Department of Chemistry, Imperial College London, London, SW7 2AZ, UK

### Satish Balasaheb Nimse

Institute for Applied Chemistry, Department of Chemistry, Hallym University, Chuncheon, 200-702, Korea

### Dilipkumar Pal

Institute of Pharmaceutical Sciences, Guru Ghasidas Vishwavidyalaya (A Central University), Koni, Bilaspur, Chhattisgarh-495009, India

### Tobias Müller

Biokatalyse & Organische Chemie, Gebouw voor Scheikunde, Afdeling Biotechnologie, Technische Universiteit Delft, Julianalaan 136, 2628BL Delft, The Netherlands

### Kristina Djanashvili

Biokatalyse & Organische Chemie, Gebouw voor Scheikunde, Afdeling Biotechnologie, Technische Universiteit Delft, Julianalaan 136, 2628BL Delft, The Netherlands

### Isabel W. C. E. Arends

Biokatalyse & Organische Chemie, Gebouw voor Scheikunde, Afdeling Biotechnologie, Technische Universiteit Delft, Julianalaan 136, 2628BL Delft, The Netherlands

### Joop A. Peters

Biokatalyse & Organische Chemie, Gebouw voor Scheikunde, Afdeling Biotechnologie, Technische Universiteit Delft, Julianalaan 136, 2628BL Delft, The Netherlands

### **Ulf Hanefeld**

Biokatalyse & Organische Chemie, Gebouw voor Scheikunde, Afdeling Biotechnologie, Technische Universiteit Delft, Julianalaan 136, 2628BL Delft, The Netherlands

### Atanu Modak

Department of Chemistry, Indian Institute of Technology, Powai, Mumbai, 400076, India

### Debabrata Maiti

Department of Chemistry, Indian Institute of Technology, Powai, Mumbai, 400076, India

### T. Gensch

Westfälische Wilhelms-Universität Münster, Organisch-Chemisches Institut, Corrensstrasse 40, 48149 Münster, Germany

### M. N. Hopkinson

Westfälische Wilhelms-Universität Münster, Organisch-Chemisches Institut, Corrensstrasse 40, 48149 Münster, Germany

### F. Glorius

Westfälische Wilhelms-Universität Münster, Organisch-Chemisches Institut, Corrensstrasse 40, 48149 Münster, Germany

### J. Wencel-Delord

Laboratoire de Chimie Moléculaire (UMR CNRS 7509), Université de Strasbourg, ECPM 25 Rue Becquerel, 67087 Strasbourg, France

### Nicole M. G. Franssen

Van't Hoff Institute for Molecular Sciences (HIMS), Universiteit van Amsterdam, Science Park 904, 1098 XH Amsterdam, The Netherlands. Dutch Polymer Institute DPI, 5600 AX Eindhoven, The Netherlands

### Joost N. H. Reek

Van't Hoff Institute for Molecular Sciences (HIMS), Universiteit van Amsterdam, Science Park 904, 1098 XH Amsterdam, The Netherlands

### Bas de Bruin

Van't Hoff Institute for Molecular Sciences (HIMS), Universiteit van Amsterdam, Science Park 904, 1098 XH Amsterdam, The Netherlands.

### Mark D. Greenhalgh

School of Chemistry, University of Edinburgh, Joseph Black Building, West Mains Road, Edinburgh, EH9 3JJ, UK

### Stephen P. Thomas

School of Chemistry, University of Edinburgh, Joseph Black Building, West Mains Road, Edinburgh, EH9 3JJ, UK

### Kenichi Horisawa

Division of Organogenesis and Regeneration, Department of Molecular and Cellular Biology, Medical Institute of Bioregulation, Kyushu University, Fukuoka, Japan

### **Preface**

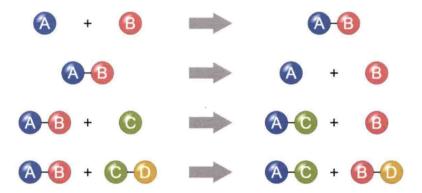
Chemical reactions are processes that transform chemical substances to create new substances with different identities. Traditionally, these processes involve solely the movement of electrons in forming and breaking bonds between atoms; processes that change the composition of nuclei are nuclear reactions. Equations are often used to represent the path from starting materials to end products, and provide details such as reaction conditions, stoichiometry, and intermediates. In a chemical equation, the number of atoms for each species must be equal on either side of the arrow, which indicates the direction in which the reaction proceeds. Reversible reactions are denoted by double arrows, which means the forward and reverse reactions will compete with each other until the system reaches equilibrium. The simplest form of a chemical reaction—in which reactants are converted into products in a single step with a single transition state—are known as elementary reactions. Although more commonly, reactions take place in a single phase, in certain cases, they occur at the interface between two different states (e.g. solid/gas interface).

Depending on the specific conditions, a chemical reaction can proceed under thermodynamic or kinetic control. A thermodynamically favored reaction is one where the products are more stable than the reactants (i.e. energy state of products is lower than that of reactants), resulting in the release of energy or heat (exothermic). On the other hand, a reaction is kinetically favored when the activation energy is low (i.e. low energy transition state), leading to faster reaction rates. Catalysts can lower the intrinsic activation energy of a reaction and thus speed it up. Generally speaking, thermodynamic and kinetic variables both need to be taken into account in determining whether or not a chemical reaction is favorable. There are four basic reaction types: synthesis, decomposition, single replacement, and double replacement. Synthesis refers to bond-forming reactions in which two or more simple substances combine into a more complex substance. Decomposition is the reverse of a synthesis reaction, involving the breakage of bonds in a complex substance to form simpler ones. Single replacement reactions involve the exchange of a single, uncombined element for another within a compound, while double replacement reactions involve a switch between two elements that are both within compounds. Reactions that lead to a change in oxidation states of atoms are classified as either oxidation or reduction reactions ("redox"). Photochemical reactions are ones that are catalyzed by light energy. Acid-base reactions involve the transfer of protons from the acidic species to the basic species. In organic chemistry, reactions are generally classified according to their mechanism (movement of electrons). In substitution reactions, a functional group is replaced by another group (the "nucleophile") in a compound. Elimination reactions lead to the loss of a functional group from a compound via the formation of a C=C double bond. By contrast, rearrangement reactions give rise to changes in the carbon skeleton, often resulting in structural isomers. Other organic reactions include radical reactions, oxidations/reductions, condensations, hydrolysis, polymerizations, among many others. Many molecules will have more than one reactive site - much research effort in synthetic chemistry has been put into developing conditions and catalysts that will selectively or specifically functionalize one site over another. Chemical reactions lie at the core of biological, industrial, and many other important processes. This book aims to provide a general overview of the type, mechanism, and application of chemical reactions.

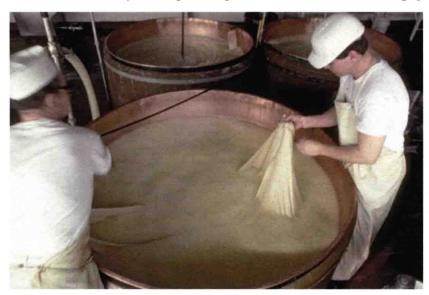
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### INTRODUCTION

Chemical reaction a process in which one or more substances, the reactants, are converted to one or more different substances, the products. Substances are either chemical elements or compounds. A chemical reaction rearranges the constituent atoms of the reactants to create different substances as products.



Chemical reactions are an integral part of technology, of culture, and indeed of life itself. Burning fuels, smelting iron, making glass and pottery, brewing beer, and making wine and cheese are among many examples of activities incorporating chemical reactions that have been known and used for thousands of years. Chemical reactions abound in the geology of Earth, in the atmosphere and oceans, and in a vast array of complicated processes that occur in all living systems.



Chemical reactions must be distinguished from physical changes. Physical changes include changes of state, such as ice melting to water and water evaporating to vapour. If a physical change occurs, the physical properties of a substance will change, but its chemical identity will remain the same. No matter what its physical state, water (H<sub>2</sub>O) is the same compound, with each molecule composed of two atoms of hydrogen and one atom of oxygen. However, if water, as ice, liquid, or vapour, encounters sodium metal (Na), the atoms will be redistributed to give the new substances molecular hydrogen (H<sub>2</sub>) and sodium hydroxide (NaOH). By this, we know that a chemical change or reaction has occurred.

### Historical Overview

The concept of a chemical reaction dates back about 250 years. It had its origins in early experiments that classified substances as elements and compounds and in theories that explained these processes. Development of the concept of a chemical reaction had a primary role in defining the science of chemistry as it is known today.

The first substantive studies in this area were on gases. The identification of oxygen in the 18th century by Swedish chemist Carl Wilhelm Scheele and English clergyman Joseph Priestley had particular significance. The influence of French chemist Antoine-Laurent Lavoisier was especially notable, in that his insights confirmed the importance of quantitative measurements of chemical processes. The concept of chemical reactions involving the combination of elements clearly emerged from his writing, and his approach led others to pursue experimental chemistry as a quantitative science.

The other occurrence of historical significance concerning chemical reactions was the development of atomic theory. For this, much credit goes to English chemist John Dalton, who postulated his atomic theory early in the 19th century. Dalton maintained that matter is composed of small, indivisible particles, that the particles, or atoms, of each element were unique, and that chemical reactions were involved in rearranging atoms to form new substances. This view of chemical reactions accurately defines the current subject. Dalton's theory provided a basis for understanding the results of earlier experimentalists, including the law of conservation of matter (matter is neither created nor destroyed) and the law of constant composition (all samples of a substance have identical elemental compositions).

Thus, experiment and theory, the two cornerstones of chemical science in the modern world, together defined the concept of chemical reactions. Today experimental chemistry provides innumerable examples, and theoretical chemistry allows an understanding of their meaning.

### Synthesis

When making a new substance from other substances, chemists say either that they carry out a synthesis or that they synthesize the new material. Reactants are converted to products, and the process is symbolized by a chemical equation. For example, iron (Fe) and sulfur (S) combine to form iron sulfide (FeS).

$$Fe(s) + S(s) \rightarrow FeS(s)$$

The plus sign indicates that iron reacts with sulfur. The arrow signifies that the reaction "forms" or "yields" iron sulfide, the product. The state of matter of reactants and products is designated with the symbols (s) for solids, (l) for liquids, and (g) for gases.

### The Conservation of Matter

In reactions under normal laboratory conditions, matter is neither created nor destroyed, and elements are not transformed into other elements. Therefore, equations depicting reactions must be balanced; that is, the same number of atoms of each kind must appear on opposite sides of the equation. The balanced equation for the iron-sulfur reaction shows that one iron atom can react with one sulfur atom to give one formula unit of iron sulfide.

Chemists ordinarily work with weighable quantities of elements and compounds. For example, in the iron-sulfur equation the symbol Fe represents 55.845 grams of iron, S represents 32.066 grams of sulfur, and FeS represents 87.911 grams of iron sulfide. Because matter is not created or destroyed in a chemical reaction, the total mass of reactants is the same as the total mass of products. If some other amount of iron is used, say, one-tenth as much (5.585 grams), only one-tenth as much sulfur can be consumed (3.207 grams), and only one-tenth as much iron sulfide is produced (8.791 grams). If 32.066 grams of sulfur were initially present with 5.585 grams of iron, then 28.859 grams of sulfur would be left over when the reaction was complete.

The reaction of methane ( $CH_4$ , a major component of natural gas) with molecular oxygen ( $O_2$ ) to produce carbon dioxide ( $CO_2$ ) and water can be depicted by the chemical equation

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$$

Here another feature of chemical equations appears. The number 2 preceding  $O_2$  and  $H_2O$  is a stoichiometric factor. (The number 1 preceding  $CH_4$  and  $CO_2$  is implied.) This indicates that one molecule of methane reacts with two molecules of oxygen to produce one molecule of carbon dioxide and two molecules of water. The equation is balanced because the same number of atoms of each element appears on both sides of the equation (here one carbon, four hydrogen, and four oxygen atoms). Analogously with the iron-sulfur example, we can say that 16 grams of methane and 64 grams of oxygen will produce 44 grams of carbon dioxide and 36 grams of water. That is, 80 grams of reactants will lead to 80 grams of products.

The ratio of reactants and products in a chemical reaction is called chemical stoichiometry. Stoichiometry depends on the fact that matter is conserved in chemical processes, and calculations giving mass relationships are based on the concept of the mole. One mole of any element or compound contains the same number of atoms or molecules, respectively, as one mole of any other element or compound. By international agreement, one mole of the most common isotope of carbon (carbon-12) has a mass of exactly 12 grams (this is called the molar mass) and represents  $6.022140857 \times 10^{23}$  atoms (Avogadro's number). One mole of iron contains 55.847 grams; one mole of methane contains 16.043 grams; one mole of molecular oxygen is equivalent to 31.999 grams; and one mole of water is 18.015 grams. Each of these masses represents  $6.022140857 \times 10^{23}$  molecules.

### **Energy Considerations**

Energy plays a key role in chemical processes. According to the modern view of chemical reactions, bonds between atoms in the reactants must be broken, and the atoms or pieces of molecules are reassembled into products by forming new bonds. Energy is absorbed to break bonds, and energy is evolved as bonds are made. In some reactions the energy required to break bonds is larger than the energy evolved on making new bonds, and the net result is the absorption of energy. Such a reaction is said to be endothermic if the energy is in the form of heat. The opposite of endothermic is exothermic; in an exothermic reaction, energy as heat is evolved. The more general terms exoergic (energy evolved) and endoergic (energy required) are used when forms of energy other than heat are involved.

A great many common reactions are exothermic. The formation of compounds from the constituent elements is almost always exothermic. Formation of water from molecular hydrogen and oxygen and the formation of a metal oxide such as calcium oxide (CaO) from calcium metal and oxygen gas are examples. Among widely recognizable exothermic reactions is the combustion of fuels.

The formation of slaked lime (calcium hydroxide, Ca(OH),) when water is added to lime (CaO) is exothermic.

$$CaO(s) + H_2O(l) \rightarrow Ca(OH)_2(s)$$

This reaction occurs when water is added to dry portland cement to make concrete, and heat evolution of energy as heat is evident because the mixture becomes warm.

Not all reactions are exothermic (or exoergic). A few compounds, such as nitric oxide (NO) and hydrazine (N<sub>2</sub>H<sub>4</sub>), require energy input when they are formed from the elements. The decomposition of limestone (CaCO<sub>3</sub>) to make lime (CaO) is also an endothermic process; it is necessary to heat limestone to a high temperature for this reaction to occur.

$$CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$$

The decomposition of water into its elements by the process of electrolysis is another endoergic process. Electrical energy is used rather than heat energy to carry out this reaction.

$$2 H_2O(g) \rightarrow 2 H_2(g) + O_2(g)$$

Generally, evolution of heat in a reaction favors the conversion of reactants to products. However, entropy is important in determining the favorability of a reaction. Entropy is a measure of the number of ways in which energy can be distributed in any system. Entropy accounts for the fact that not all energy available in a process can be manipulated to do work.

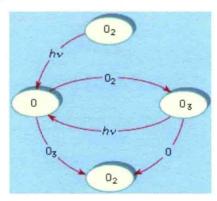
A chemical reaction will favor the formation of products if the sum of the changes in entropy for the reaction system and its surroundings is positive. An example is burning wood. Wood has a low entropy. When wood burns, it produces ash as well as the high-entropy substances carbon dioxide gas and water vapor. The entropy of the reacting system increases during combustion. Just as important, the heat energy transferred by the combustion to its surroundings increases the entropy in the surroundings. The total of entropy changes for the substances in the reaction and the surroundings is positive, and the reaction is product-favored.

When hydrogen and oxygen react to form water, the entropy of the products is less than that of the reactants. Offsetting this decrease in entropy, however, is the increase in entropy of the surroundings owing to the heat transferred to it by the exothermic reaction. Again because of the overall increase in entropy, the combustion of hydrogen is product-favored.

### Kinetic Considerations

Chemical reactions commonly need an initial input of energy to begin the process. Although the combustion of wood, paper, or methane is an exothermic process, a burning match or a spark is needed to initiate this reaction. The energy supplied by a match arises from an exothermic chemical reaction that is itself initiated by the frictional heat generated by rubbing the match on a suitable surface.

In some reactions, the energy to initiate a reaction can be provided by light. Numerous reactions in Earth's atmosphere are photochemical, or light-driven, reactions initiated by solar radiation. One example is the transformation of ozone  $(O_3)$  into oxygen  $(O_2)$  in the troposphere. The absorption of ultraviolet light (hv) from the Sun to initiate this reaction prevents potentially harmful high-energy radiation from reaching Earth's surface.



For a reaction to occur, it is not sufficient that it be energetically product-favored. The reaction must also occur at an observable rate. Several factors influence reaction rates, including the concentrations of reactants, the temperature, and the presence of catalysts. The concentration affects the rate at which reacting molecules collide, a prerequisite for any reaction. Temperature is influential because reactions occur only if collisions between reactant molecules are sufficiently energetic. The proportion of molecules with sufficient energy to react is related to the temperature. Catalysts affect rates by providing a lower energy pathway by which a reaction can occur. Among common catalysts are precious metal compounds used in automotive exhaust systems that accelerate the breakdown of pollutants such as nitrogen dioxide into harmless nitrogen and oxygen. A wide array of biochemical catalysts are also known, including chlorophyll in plants (which facilitates the reaction by which atmospheric carbon dioxide is converted to complex organic molecules such as glucose) and many biochemical catalysts called enzymes. The enzyme pepsin, for example, assists in the breakup of large protein molecules during digestion.

### Classifying Chemical Reactions

Chemists classify reactions in a number of ways: (a) by the type of product, (b) by the types of reactants, (c) by reaction outcome, and (d) by reaction mechanism. Often, a given reaction can be placed in two or even three categories.

### Classification by Type of Product

### **Gas-forming Reactions**

Many reactions produce a gas such as carbon dioxide, hydrogen sulfide (H<sub>2</sub>S), ammonia (NH<sub>3</sub>), or sulfur dioxide (SO2). An example of a gas-forming reaction is that which occurs when a metal carbonate such as calcium carbonate (CaCO<sub>3</sub>, the chief component of limestone, seashells, and marble) is mixed with hydrochloric acid (HCl) to produce carbon dioxide.

$$CaCO_3(s) + 2 HCl(aq) \rightarrow CaCl_2(aq) + CO_2(g) + H_2O(l)$$

In this equation, the symbol (aq) signifies that a compound is in an aqueous, or water, solution.

Cake-batter rising is caused by a gas-forming reaction between an acid and baking soda, sodium hydrogen carbonate (sodium bicarbonate, NaHCO<sub>3</sub>). Tartaric acid ( $C_4H_6O_6$ ), an acid found in many foods, is often the acidic reactant.

$$C_4H_5O_6(aq) + NaHCO_3(aq) \rightarrow NaC_4H_5O_6(aq) + H_2O(1) + CO_2(g)$$

In this equation, NaC<sub>4</sub>H<sub>5</sub>O<sub>6</sub> is sodium tartrate.



Most baking powders contain both tartaric acid and sodium hydrogen carbonate, which are kept apart by using starch as a filler. When baking powder is mixed into the moist batter, the acid and sodium hydrogen carbonate dissolve slightly, which allows them to come into contact and react. Carbon dioxide is produced, and the batter rises.

### **Precipitation Reactions**

Formation of an insoluble compound will sometimes occur when a solution containing a particular cation (a positively charged ion) is mixed with another solution containing a particular anion (a negatively charged ion). The solid that separates is called a precipitate.