

KINETICS OF CHEMICAL REACTIONS IN FOODS

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Summary

Multiple chemical reactions take place in foods. While some reactions are necessary to produce the compounds responsible for flavor, texture, and nutritional value, others result in spoilage or undesirable, harmful substances. Chemical reactions occur when sufficient energy is brought to the molecules of one or several compounds in proximity of each other, producing collisions that result in breakage or formation of bonds among the atoms in those molecules. Chemical kinetics studies the rate at which chemical reactions take place and establishes mathematical relationships and mechanisms describing such phenomena. In homogeneous systems, rates of reaction are mainly dictated by temperature, concentration, and the nature of the reactants. In heterogeneous systems, rates of reaction can be limited by the rates of heat and mass transfer. Rates of reaction can also be modified by the addition of catalysts. The most important chemical reactions in food systems are lipid oxidations, chain reactions that cause rancidity in oil and fat-containing foods, and non-enzymatic browning reactions of amines and reducing sugars. The main variables studied in the chemical kinetics of food systems are reagent concentration, temperature, pH, and water activity. The use of enzymes to catalyze reactions in the food industry is increasing. Most kinetic studies of foods are empirical, due to the difficulty in measuring the concentrations of multiple reactant species present in foods which are usually complex and heterogeneous. As instrumentation and computer power increases, the ability to measure concentrations rapidly and accurately in complex mixtures will facilitate quantification of reaction kinetics. New non-thermal technologies that use, for example, high pressure or electromagnetic fields to inactivate microorganisms, also produce chemical changes in foods. Thermodynamics and kinetics of chemical reactions under these unusual conditions must be studied.

1. Introduction

Foods are generally composed of several chemical and biochemical compounds that, by being exposed to each other or the environment, react, resulting in new compounds. Some of these reactions are driven by natural processes that may be intrinsic to their metabolism, as in the growing and ripening of fruits and vegetables, or may be caused by external agents such as micro-organisms like yeast or bacteria, producing spoilage. Also, foods often undergo simple industrial processing, as in packaging, or more

complex processes like wine brewing, bread making, or “prepared meal” making (See *Food Process Engineering*). During these processes, many simultaneous or sequential chemical or biochemical reactions occur. Design of food processes and the selection and specification of equipment requires a thorough understanding of transport phenomena, chemical kinetics, and thermodynamics. While thermodynamics deals with the exchange of energy in a chemical or physical process and the equilibrium and spontaneity of such processes (see *Food Engineering Thermodynamics*), chemical kinetics studies the rates of chemical changes taking place within thermodynamic limitations. The study of chemical kinetics plays an important role in the preservation, preparation, and analysis of foods. For food preservation, it is necessary to determine the optimum conditions required to decrease the rate of degradation, in other words, to decrease the rate at which certain compounds react within a food during storage. Conversely, to increase food productivity, preparation requires that reactions among food components take place in the shortest possible time, resulting in safe, consumer-acceptable products. In other words, it is necessary to find those processing conditions that can maximize the rates at which desired reactions occur, and thus minimize those of undesirable reactions. Finally, the chemical analysis of foods frequently involves chemical reactions in which the kinetics is closely related to the concentration of a species of interest.

In a homogeneous system, where all species are in the same phase, the rate of chemical reactions taking place depends on the concentration of the reactants, and the temperature and pressure conditions. Difficulty in studying chemical kinetics increases with the number of reactants in a mixture, the presence of competing reactions, and the frequent lack of knowledge of reaction mechanisms. In addition, when reactants are in different phases, that is, when the system is heterogeneous, the rate of reaction may be affected by the rate at which a species in one phase migrates to the phase where the reaction is taking place. Chemical reactions may be endothermic or exothermic; that is, they may absorb or release energy. Therefore, because of their temperature dependence, reaction rates may be constrained by heat transfer characteristics of the reaction system. Also, catalysts exist, which are compounds that in small quantities affect the rate of some reactions but remain chemically unaffected themselves. The mechanism of action and the effects of non-biological catalysts have been widely studied in chemical process industries, but their application to food processing is limited because compared to enzymes, their biological counterparts, they may be toxic or inefficient. Although the role of enzymes in metabolism and their mechanism of action are not always well understood, they play a most important role in the transformation of biological systems. Their application to food processing and analysis is widespread.

The objectives of this article are to present the fundamentals of chemical kinetics in foods and the mathematical representation of rates of reaction during food processing and storage. Non-enzymatic browning and lipid autoxidation, probably the most studied reactions in foods, are presented in more detail than other reactions because of their importance to food processing. Empirical kinetic models used to determine rates of change of quality attributes, rather than chemical composition, are presented. The last part of this article is devoted to enzyme kinetics in foods and food processing. Many of the chemical reactions occurring in food systems are heterogeneous and require careful consideration of mass transfer and diffusion. The combined analysis of reaction rates

coupled with mass transfer is beyond the scope of this article.

2. Fundamental Concepts

Chemical kinetics deals with the rate at which chemical reactions take place. A chemical reaction occurs when sufficient energy is present in one or more molecules to produce rupture or formation of covalent bonds among atoms of these molecules when they are in proximity. Therefore, at the molecular level, chemical kinetics deals with the rate at which energy is brought to a molecule to react. The study of chemical kinetics is entirely based on the “law of mass action”, published in 1864 by Guldberg and Waage. The law of mass action states that the rate r at which a chemical reaction occurs is a function of the mass of the chemical species (e.g., M and N) present in a mixture (i.e., $r = \alpha M^a N^b$). The effect of temperature on reaction rates was first studied by Van't Hoff in 1884 and by Arrhenius in 1889. Interpretation of Arrhenius parameters was made through the “collision theory” and then by Eyring in 1935 through the “theory of absolute reaction rates”. Although great progress has been made in elucidating molecular interactions and their effect on chemical kinetics, most kinetic studies today deal with an empirical approach in the determination of parameters from these early equations.

2.1. Rate of Reaction

Rate of reaction is defined as the rate of change in the number of molecules of a given reactant or product per unit volume with respect to time. The number of molecules is most commonly represented as the number of moles (6.02×10^{23} molecules per mole). Consider A reacting with B to produce C: $aA + bB \rightarrow cC$. The rate of reaction is given by:

$$r_A = -\frac{1}{a \cdot V} \frac{dN_A}{dt} \text{ or} \quad (1)$$

$$r_B = -\frac{1}{b \cdot V} \frac{dN_B}{dt} \text{ or} \quad (2)$$

$$r_C = \frac{1}{c \cdot V} \frac{dN_C}{dt} \text{ and} \quad (3)$$

$$r_A = r_B = r_C \quad (4)$$

where r_A , r_B and r_C are the rates of reaction with respect to species A, B, and C, respectively; a , b , and c are the stoichiometric coefficients for A, B, and C, respectively; and N_A , N_B and N_C represent the number of moles of A, B, and C, respectively. V represents the volume containing the reaction mixture and t represents time. Note that the rate of reaction is always positive, which explains the minus sign when the concentration of a reactant decreases and the positive sign when it increases. If the volume is constant, the rate of reaction can be expressed as the activities of the components in the solution:

$$r_A = -\frac{da_A}{dt} = -\frac{d\gamma_A C_A}{dt} \text{ or} \quad (5)$$

$$r_B = -\frac{1}{2} \frac{da_A}{dt} - \frac{1}{2} \frac{d\gamma_B C_B}{dt} \text{ or} \quad (6)$$

$$r_C = \frac{da_C}{dt} = \frac{d\gamma_C C_C}{dt} \quad (7)$$

where a_A , a_B , and a_C are the activities, γ_A , γ_B , and γ_C the activity coefficients, and C_A , C_B , and C_C the concentrations of A, B, and C, respectively. When possible, activities (not concentrations) should be used in determining rates of reaction, because not all molecules of the species are available for reaction. However, in dilute solutions with low ionic strength activity, coefficients are nearly equal to one, allowing the use of concentrations in the calculation of reaction rates. Therefore, in an ideal homogeneous system, the rate of reaction is only a function of temperature, pressure, and composition of reacting species. Because pressure and temperature are interrelated, the rate of reaction can only be expressed as a function of temperature and composition. From experimental observations, and based on the law of mass action and the collision theory, it was found that the rate of reaction could often be expressed as:

$$r = kC_A^{a'}C_B^{b'} \quad (8)$$

where k is a proportionality factor called the rate coefficient, or rate constant, which is independent of the concentration of the species, but is a function of temperature. The powers a' and b' are called partial orders with respect to A and B, respectively. The overall order of the reaction is equal to the sum of the partial orders.

2.2. Order of Reaction

The partial orders of the reactions coincide with the molecularity of elementary processes. Otherwise, they must be determined experimentally. In other words, for non-elementary reactions, Equation (8) is a semi-empirical relation. Theoretically, all processes could be decomposed into elementary reactions and the true order with respect to each of the species involved in the reaction could be determined. However, it is very difficult to elucidate the mechanism of reactions that involve several steps and/or several reactants reacting sequentially or simultaneously, and often too fast to be detected with available technology. There exist different approaches to determining the orders of reaction and the specific rate constant. These may be found in references presented at the end of this article.

2.3. Effect of Temperature

The effect of temperature on the rate of reaction is accounted for in the specific rate constant and is given by the Arrhenius equation:

$$k = Ae^{\left(\frac{-E_a}{RT}\right)} \quad (9)$$

where A is the pre-exponential or frequency factor, E_a is the activation energy, R is the ideal gas constant, and T is the absolute temperature at which the reaction is taking place. This equation is based on the assumptions that 1) molecules undergoing chemical changes are in a given state called the active state, 2) the active molecules are in a higher energetic state than normal molecules, 3) active molecules are in extremely small proportion compared to normal ones and, 4) active and normal molecules are in equilibrium.

Once A and E_a are known, along with the partial orders of the reaction, the determination of the reaction rate as a function of temperature and reactants concentration becomes possible. Knowing the partial orders of reaction and the concentration of reactants, experimental determination of k at different temperatures and the linearization of the Arrhenius equation allows the determination of A and E_a .

2.4. Activation Energy and Frequency Factor

The activation energy corresponds to the energy necessary for a molecule to become active and therefore react. The variation of energy during a reaction is represented in Figure 1.

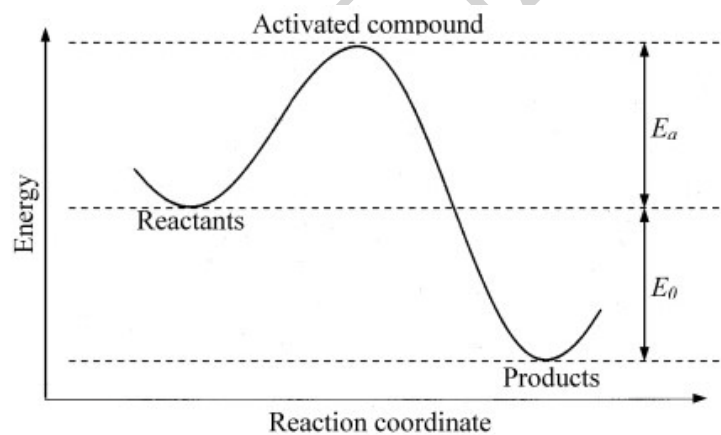
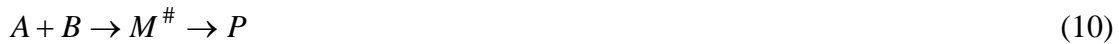


Figure 1. Change of free energy during the course of a chemical reaction.

From the collision theory, the term $(-E_a/RT)$ represents the fraction of collisions having energy greater than E_a ; the frequency factor would represent the number of collisions. This theory is not always valid because not all collisions are sufficiently energetic to result in products. It appears that an orientation factor needs to be included. On the other hand, the theory of absolute reaction rates, based on the assumption of equilibrium between activated and normal molecules, provides a better interpretation of the frequency factor.

Consider for example the following reaction:



where $M^{\#}$ and P represent the activated complex products, respectively; the frequency factor is given by:

$$A = \nu \frac{f_{\#}}{f_A f_B} \quad (11)$$

where ν is the frequency of vibration that leads to the dissociation of the active complex $M^{\#}$ into products. $f_{\#}$, f_A , and f_B are partitioning functions that represent the energy possessed by the molecules of $M^{\#}$, A, and B, respectively. Energy given to a molecule is distributed among its degrees of freedom. These degrees of freedom may be grouped as translational, rotational, vibrational, electronic, and nuclear. Further details on the estimation of partitioning functions can be found elsewhere. Although in common experimental temperature ranges, the frequency factor is not considerably affected by temperature; in fact, it is a function of temperature.

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Biographical Sketches

José I. Reyes De Corcuera received a B.S. in Chemical Engineering from the Universidad Nacional Autónoma de México in 1994. In 1996, he was awarded a Fulbright-CONACyT (National Council for Science and Technology, México) scholarship to pursue graduate studies at Washington State University where he received a M.S. in Chemical Engineering in 1998 and where he is currently pursuing Ph.D. studies. He worked as project engineer for CPI-Südmo, Mexico. His current research focuses on the stabilization of enzyme-based electrochemical biosensors.

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