

Molecular Gastronomy: A New Emerging Scientific Discipline

Peter Barham,^{†,‡} Leif H. Skibsted,[‡] Wender L. P. Bredie,[‡] Michael Bom Frøst,[‡] Per Møller,[‡] Jens Risbo,[‡]
Pia Snitkjær,[‡] and Louise Mørch Mortensen[‡]

Department of Physics, University of Bristol, H. H. Wills Physics Laboratory, Tyndall Avenue, Bristol, United Kingdom BS8 1TL and Department of Zoology, University of Cape Town, Rondebosch, 7701 Cape Town, South Africa and Department of Food Science, University of Copenhagen, Rolighedsvej 30, DK-1958, Frederiksberg, Denmark

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1. Introduction

The science of domestic and restaurant cooking has recently moved from the playground of a few interested amateurs into the realm of serious scientific endeavor. A number of restaurants around the world have started to adopt a more scientific approach in their kitchens,^{1–3} and perhaps partly as a result, several of these have become acclaimed as being among the best in the world.^{4,5}

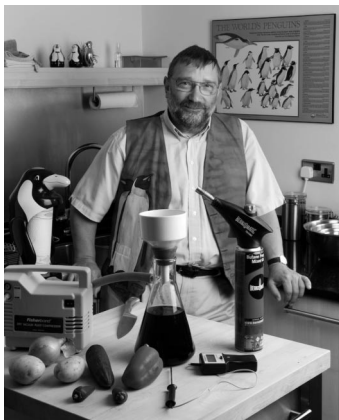
Today, many food writers and chefs, as well as most gourmets, agree that chemistry lies at the heart of the very finest food available in some of the world's finest restaurants. At least in the world of gourmet food, chemistry has managed to replace its often tarnished image with a growing respect as the application of basic chemistry in the kitchen has provided the starting point for a whole new cuisine. The application of chemistry and other sciences to restaurant and domestic cooking is thus making a positive impact in a very public arena which inevitably gives credence to the subject as a whole.

As yet, however, this activity has been largely in the form of small collaborations between scientists and chefs. To date, little “new science” has emerged, but many novel applications of existing science have been made, assisting chefs to produce new dishes and extend the range of techniques available in their kitchens. Little of this work has appeared in the scientific literature,^{2,3,6–9} but the work has received an enormous amount of media attention. A quick Google search

* To whom correspondence should be addressed. E-mail: Peter.Barham@bristol.ac.uk.

[†] University of Bristol and University of Cape Town.

[‡] University of Copenhagen.



Peter Barham is a Professor of Physics at Bristol University U.K., honorary Professor of Molecular Gastronomy in the Life Sciences faculty of the University of Copenhagen, and honorary Research Associate at the Animal Demography Unit in Zoology at the University of Cape Town. In Bristol, in addition to carrying out his own original research in fundamental Polymer Physics and in the conservation of penguins, he is involved in undergraduate and postgraduate teaching and a range of administrative tasks. In Cape Town he is involved with a group trying to save the endangered African penguins. In Copenhagen, he is helping to create research and teaching activities in the new and emerging area of Molecular Gastronomy. His book "The science of cooking", published in 2001 by Springer, is not only popular with the general public but also used as a text in many catering colleges. In the past few years Peter has been collaborating with a number of chefs (notably Heston Blumenthal of the Fat Duck) with the idea of bringing science more closely into the kitchen, both at home and in the restaurant. In 2003 he was awarded the 2003 Kelvin Medal by the Institute of Physics for his contributions to the promotion of the public awareness of science.



Leif H. Skibsted received his M. Pharm. degree from the Royal Danish School of Pharmacy in 1972 and obtained his Ph.D. degree in Inorganic Chemistry in 1976. Since 1974 he has been with the Royal Veterinary and Agricultural University, which merged into the University of Copenhagen in 2007. Following mechanistic studies of iron-catalyzed oxidation reactions in meat and light-induced degradation of plant pigments, he was appointed Professor of Food Chemistry in 1992. His current research interests include high-pressure effects on proteins, the mechanism of antioxidant interaction as studied by ESR and laser-flash spectroscopy, radical chemistry of meat pigments, and molecular gastronomy. Among the several awards he has received are the Niels and Ellen Bjerrum Award and Gold Medal in Chemistry, Carlsberg Award in Agricultural Science, and Ole Roemer Research Award. Since 2006 he has had the status as a "highly cited" author in the ISI Web of Knowledge.

will reveal thousands of news articles over the past few years; a very few recent examples can be found in China,¹⁰ the United States,^{11,12} and Australia.¹³

In this review we bring together the many strands of chemistry that have been and are increasingly being used in the kitchen to provide a sound basis for further developments



Wender L. P. Bredie (born 1966) is Professor of Sensory Science at the Department of Food Science, Faculty of Life Sciences, the University of Copenhagen. He is a food science engineer (M.Sc.) from Wageningen University (The Netherlands) and holds a first class Ph.D. in Flavour Chemistry from The University of Reading (U.K.). Since 1991 he has been working in research and education within sensory and flavor science. He became head of the sensory science research group in 2003 and was appointed as Professor in 2006. His research has been addressing the chemistry behind aromas and tastes in foods and the relationships with sensory perception and physiology. He has worked extensively on descriptive sensory analysis methodology and studied relationships between descriptive sensory, affective, and product instrumental variables using multivariate modeling. He has been co-organizer of the 11th Weurman Flavour Research Symposium (2005) and is Editor of the book *Flavour Science: Recent advances and trends* (2006).



Michael Bom Frøst is Associate Professor at the Sensory Science group. He received his Ph.D. degree in Sensory Science in 2002 working with Professor Magni Martens on the sensory properties of low-fat dairy products, their relationships to consumer perception, and processing parameters. Following this work, he continued this researching the coveted sensory property 'creaminess' in low-fat dairy products, including the relationship to physical and chemical properties. Since the beginning of 2007 he has worked on a research project on Molecular Gastronomy at the Food Science Department. He also directs the M.Sc. education in Gastronomy and Health.

in the area. We also attempt throughout to show using relevant illustrative examples how knowledge and understanding of chemistry can be applied to good effect in the domestic and restaurant kitchen.

Our basic premise is that the application of chemical and physical techniques in some restaurant kitchens to produce novel textures and flavor combinations has not only revolutionized the restaurant experience but also led to new enjoyment and appreciation of food. Examples include El Bulli (in Spain) and the Fat Duck (in the United Kingdom), two restaurants that since adopting a scientific approach to cooking have become widely regarded as among the finest



Per Møller was educated in physics and mathematics at the University of Copenhagen (M.Sc.). He later received his M.A. degree in Psychology and Ph.D. degree in Cognitive Science from the University of Rochester, Rochester, NY.. He works on psychological and neurological problems of the senses using psychophysical and neurophysiological methods. Among other problems he works on relationships between the senses, reward, and appetite.



Pia Snitkjær was born in Denmark in 1977. She obtained her Masters degree in Food Science from the Royal Veterinary and Agricultural University of Denmark in 2005. Since 2006 she has been a Ph.D. student in the emerging field of Molecular Gastronomy. She is studying the fundamentals of stock reduction using sensory and chemical analysis. In addition, she has been a key person in establishing gastronomy as a teaching field at the University of Copenhagen.



Jens Risbo is Associate Professor of Food Chemistry and was born 1969 in Virum, Denmark. He graduated from the Technical University of Denmark with his Master of Science degree (1994) in Chemical Engineering and Ph.D. degree (1997) within the experimental and theoretical physical chemistry of phospholipid membranes. His research interests are within food material science, phase transitions in foods, and transport phenomena. He has recently taken up an interest in the physical chemistry related to gastronomy.

in the world. All this begs the fundamental question: why should these novel textures and flavors provide so much real pleasure for the diners?

Such questions are at the heart of the new science of Molecular Gastronomy. The term Molecular Gastronomy has gained a lot of publicity over the past few years, largely because some chefs have started to label their cooking style as Molecular Gastronomy (MG) and claimed to be bringing the use of scientific principles into the kitchen. However, we should note that three of the first chefs whose food was “labeled” as MG have recently written a new manifesto protesting against this label.¹⁴ They rightly contend that what is important is the finest food prepared using the best available ingredients and using the most appropriate methods (which naturally includes the use of “new” ingredients, for example, gelling agents such as gellan or carageenan, and processes, such as vacuum distillation, etc.).

We take a broad view of Molecular Gastronomy and argue it should be considered as the scientific study of why some food tastes terrible, some is mediocre, some good, and



Louise Mørch Mortensen was born in 1973. In 2001, she obtained her Masters degree in Food Science and Technology from The Royal Veterinary and Agricultural University of Denmark. Subsequently, she was employed by a manufacturer of analytical instruments, performing a range of tasks related to spectroscopy, multivariate calibrations, and compositional food analysis. She is currently working as one of the first Ph.D. students in Molecular Gastronomy. She is carrying out a project on the topic of low-temperature cooking of meat, studying the relationship between preparation time and temperature, structural changes, and sensory characteristics. Apart from her research project, she has participated in establishing teaching in gastronomy at the University of Copenhagen.

occasionally some absolutely delicious. We want to understand what it is that makes one dish delicious and another not, whether it be the choice of ingredients and how they were grown, the manner in which the food was cooked and presented, or the environment in which it was served. All will play their own roles, and there are valid scientific enquiries to be made to elucidate the extent to which they each affect the final result, but chemistry lies at the heart of all these diverse disciplines.

The judgment of the quality of a dish is a highly personal matter as is the extent to which a particular meal is enjoyed or not. Nevertheless, we hypothesize that there are a number of conditions that must be met before food becomes truly enjoyable. These include many aspects of the flavor. Clearly, the food should have flavor; but what conditions are truly important? Does it matter, for example, how much flavor a dish has; is the concentration of the flavor molecules important? How important is the order in which the flavor

molecules are released? How does the texture affect the flavor? The long-term aims of the science of MG are not only to provide chefs with tools to assist them in producing the finest dishes but also to elucidate the minimum set of conditions that are required for a dish to be described by a representative group of individuals as enjoyable or delicious, to find ways in which these conditions can be met (through the production of raw materials, in the cooking process, and in the way in which the food is presented), and hence to be able to predict reasonably well whether a particular dish or meal would be delicious. It may even become possible to give some quantitative measure of just how delicious a particular dish will be to a particular individual.

Clearly, this is an immense task involving many different aspects of the chemical sciences: from the way in which food is produced through the harvesting, packaging, and transport to market via the processing and cooking to the presentation on the plate and how the body and brain react to the various stimuli presented.

MG is distinct from traditional Food Science as it is concerned principally with the science behind any conceivable food preparation technique that may be used in a restaurant environment or even in domestic cooking from readily available ingredients to produce the best possible result. Conversely, Food Science is concerned, in large measure, with food production on an industrial scale and nutrition and food safety.

A further distinction is that although Molecular Gastronomy includes the science behind gastronomic food, to understand gastronomy it is sometimes also necessary to appreciate its wider background. Thus, investigations of food history and culture may be subjects for investigation within the overall umbrella of Molecular Gastronomy.

Further, gastronomy is characterized by the fact that strong, even passionate feelings can be involved. Leading chefs express their own emotions and visions through the dishes they produce. Some chefs stick closely to tradition, while others can be highly innovative and even provocative. In this sense gastronomy can be considered as an art form similar to painting and music.

In this review we begin with a short description of our senses of taste and aroma and how we use these and other senses to provide the sensation of flavor. We will show that flavor is not simply the sum of the individual stimuli from the receptors in the tongue and nose but far more complex. In fact, the best we can say is that flavor is constructed in the mind using cues taken from all the senses including, but not limited to, the chemical senses of taste and smell. It is necessary to bear this background in mind throughout the whole review so we do not forget that even if we fully understand the complete chemical composition, physical state, and morphological complexity of a dish, this alone will not tell us whether it will provide an enjoyable eating experience.

In subsequent sections we will take a walk through the preparation of a meal, starting with the raw ingredients to see how the chemical make up of even the apparently simplest ingredients such as carrots or tomatoes is greatly affected by all the different agricultural processes they may be subjected to before arriving in the kitchen.

Once we have ingredients in the kitchen and start to cut, mix, and cook them, a vast range of chemical reactions come into play, destroying some and creating new flavor compounds. We devote a considerable portion of the review to

the summary of some of these reactions. However, we must note that complete textbooks have failed to capture the complexity of many of these, so all we can do here is to provide a general overview of some important aspects that commonly affect flavor in domestic and restaurant kitchens.

In nearly all cooking, the texture of the food is as important as its flavor: the flavor of roast chicken is pretty constant, but the texture varies from the wonderfully tender meat that melts in the mouth to the awful rubber chicken of so many conference dinners. Understanding and controlling texture not only of meats but also of sauces, soufflés, breads, cakes, and pastries, etc., will take us on a tour through a range of chemical and physical disciplines as we look, for example, at the spinning of glassy sugars to produce candy-floss.

Finally, after a discussion of those factors in our food that seem to contribute to making it delicious, we enter the world of brain chemistry, and much of that is speculative. We will end up with a list of areas of potential new research offering all chemists the opportunity to join us in the exciting new adventures of Molecular Gastronomy and the possibility of collaborating with chefs to create new and better food in their own local neighborhoods. Who ever said there is no such thing as a free lunch?

2. Senses

Before we begin to look in any detail at the chemistry of food production and preparation, we should take in a brief overview of the way in which we actually sense the food we eat. Questions such as what makes us enjoy (or not) any particular food and what it is that makes one meal better than another are of course largely subjective. Nonetheless, we all share the same, largely chemical based, set of senses with which to interpret the taste, aroma, flavor, and texture of the food. In this section we will explore these senses and note how they detect the various food molecules before, during, and even after we have consumed them.

It is important to note at the outset that our experience of foods is mediated through all our senses: these include all the familiar senses (pain, touch, sight, hearing, taste, and smell) as well as the perhaps less familiar such as chemesthesis. As we will see, our senses of sight and touch can set up expectations of the overall flavor of food which can be very hard to ignore. Try eating the same food using either high-quality china plates and steel or silver cutlery or paper plates and plastic cutlery; the food seems to taste better with the perceived quality of the utensils. Equally, the color of food can affect our perception of the flavor; try eating a steak dyed blue!

However, among all the senses, the most significant for our appreciation of food remain the chemical senses which encompass taste, smell, and chemesthesis. These three distinct systems mediate information about the presence of chemicals in the environment. Taste or gustation detects chemical compounds dissolved in liquids using sensors mostly in the mouth. Smell or olfaction detects air-borne chemicals, both from the external world but also from the internalized compounds emitted from food in our oral cavity. Chemesthesis mediates information about irritants through nerve endings in the skin as well as other borders between us and the environments, including the epithelia in the nose, the eyes, and in the gut. Chemesthesis uses the same systems that inform us about touch, temperature, and pain.

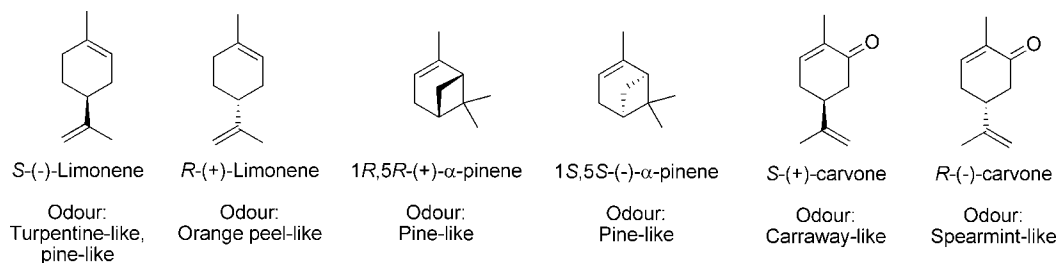


Figure 1. Molecular structures of the enantiomers of limonene, α -pinene, and carvone. The enantiomers have distinct odor characteristics (quality and threshold), which are attributed to the enantiomeric configuration. *R*(-)-Carvone is the main constituent in spearmint essential oil, and *S*(+)-carvone is the main constituent in the essential oil of caraway and dill. *R*(+)-Limonene is the main constituent of the volatile oils expressed from the fresh peel of *Citrus* spp. fruits. *S*(-)-limonene is present in the oil of fir and the needles and young twigs of *Abies alba* (Pinaceae).

2.1. Sense of Taste

Specialized chemoreceptors on the tongue, palate, soft palate, and areas in the upper throat (pharynx and laryngopharynx) detect sensations such as bitter, for example, from alkaloids, salty from many ionic compounds, sour from most acids, sweet from sugars, and umami, or savory, from some amino acids and nucleotides. Each of these taste sensations probably evolved to provide information about foods that are particularly desirable (e.g., salt, sugar, amino acids) or undesirable (e.g., toxic alkaloids). The receptors reside in taste buds mostly located in fungiform, foliate, and circumvallate but not filiform papillae on the tongue. Taste buds, as the name indicates, are bud-shaped groups of cells. Tastants, the molecules being tasted, enter a small pore at the top of the taste bud and are absorbed on microvilli at taste receptor cells.

In the past decade receptor proteins for bitter,^{15,16} sweet, and umami^{17–20} have all been identified. All these receptors are a subclass of the super family of G-protein-coupled receptors (GPCRs) and have been classified as T1R1, T1R2, T1R3, and T2Rs. The activation of GPCRs by external stimulus is the starting point of a succession of interactions between multiple proteins in the cell, leading to the release of chemical substances in the cell also called second messengers. Although the cellular signal cascade is a general pattern of GPCRs, the very large variety of each protein involved renders these mechanisms very complex so that they are under a good deal of ongoing investigation.

Taste receptors share several structural homologies with the metabotropic glutamate receptors. These receptors are composed of two main domains linked by an extracellular cystein-rich domain: a large extracellular domain (ECD) also called the “Venus Flytrap” module, due to the similarity of mechanism by which this plant traps insects, containing the ligand binding site and a seven-transmembrane domain region. Moreover, as in the case of mGluRs, T1Rs assemble as dimers at the membrane and the composition of the heterodimers has been shown to be specific to the taste recognized. Heterodimers T1R2–T1R3 are responsible for sweet sensing, whereas T1R1–T1R3 are responsible for umami tasting. A large number of T2Rs have been shown to function as bitter taste receptors in heterologous expression assays, and several have distinctive polymorphisms that are associated with significant variations in sensitivity to selective bitter tastants in mice, chimpanzees, and humans.

Receptors for sour and salty tastes are essentially ionic channels, but the identity of the salty receptor is still speculative and controversial.^{21,22} The hunt for a sour receptor has been narrowed down to a ionic channel of the type TRP,

transient receptor potential.^{21,23} Undoubtedly, more receptor proteins for other nutritionally relevant molecules will be identified. For example, recently a specific fatty acid receptor, a multifunctional CD36 glycoprotein, has been demonstrated in rats.²⁴

2.2. Sense of Smell

While the taste receptors in the mouth detect small molecules dissolved in liquids, the receptors of the olfactory system detect molecules in the air. The range of receptors provides a wide sensitivity to volatile molecules. Some of the most potent thiols can be detected in concentrations as low as 6×10^7 molecules/mL air (2-propene-1-thiol), whereas ethanol requires around 2×10^{15} molecules/mL air. Thus, there are at least 8 orders of magnitude between our sensitivity to the most and least “smelly” molecules. The sensitivity of the sense of smell varies quite significantly between individuals. Not only do different people have different sensitivity to particular aromas, some people suffer anosmia, odor blindness to specific odorants. People can be trained to become sensitive to some odorants, such as for the unpleasant smelling androstenone. To complicate the picture further, the sense of smell develops during the human lifetime; we tend to lose sensitivity at an older age, especially after the seventh decade.²⁵

An odor is detected by sensors in the nose, the odorant receptors. The way these sensors recognize aroma molecules is by “combinatorial receptor codes”, i.e., one odorant receptor recognizes a range of odorants and one odorant is recognized by a number of odorant receptors.²⁶ The distinct odor identity is created by the pattern of odorant receptors activated by the odorant’s shape. Thus, slight changes in an odorant or even in its concentration can change the identity of an odorant. A well-known example relevant to food is the distinct perceptual difference between *R*(-)- and *S*(+)-carvone, enantiomers only differing in the chirality of the compound. The two compounds are perceived as spearmint and caraway, respectively. However, by no means are all enantiomers perceived differently. For example, Laska and Tuuebner²⁷ have shown that among 10 different food-relevant enantiomers, subjects as a group were only capable of discriminating three: α -pinene, carvone, and limonene. Structures of some of these molecules are shown in Figure 1.

Linda Buck and Richard Axel were jointly awarded the Nobel Prize in Medicine and Physiology in 2004 for their discovery of “odorant receptors and the organization of the olfactory system”.²⁸ Their work has shown that each olfactory neuron expresses only one type of odorant receptor. The

odorant receptors belong to the GPCR 7TM-receptor family.²⁹ Through *in situ* hybridization of olfactory neurons in the epithelium of rats, they created an olfactory map.^{30,31} Around 1000 olfactory receptor cells, all of the same type, converge their nerve signals to distinct microdomains, glomeruli, in the olfactory bulb. This is the most direct link from the external world to the brain. From the olfactory bulb signals are relayed as patterns to other regions in the brain. Notably, there is a direct link to the amygdalae, important structures in the “limbic system”, an evolutionary old part of the brain strongly involved in human emotions. Recent work has suggested that the amygdalae not only plays important roles in evaluating affective valence of stimuli but also seem to participate in the computation and representation of perceived intensity of smells and tastes.^{32,33} The olfactory system consists of other areas in the temporal and frontal parts of the brain. The orbitofrontal cortex is of particular importance for food behavior since nerve cells in this area play a large role in the computation of hedonic properties of smell stimuli and have also been implicated in the representation of flavors of foods. Smell- and taste-sensitive neurons in the orbitofrontal cortex are also typically modulated by satiety signals and thus play a major role in determining sensory-specific satiety: the effect that appreciation for a food eaten to satiety decreases without a similar decrease in the appreciation of other foods with other sensory characteristics.³⁴

2.2.1. Perception of Aroma

Sensory scientists usually refer to smelling through the nostrils as “orthonasal perception”, whereas the aroma compounds that gain access to the olfactory epithelium through the nasopharynx (i.e., molecules released in the mouth) are referred to as being perceived retronasally. The latter is often mistakenly referred to as taste by laymen. It should perhaps more correctly be referred to as flavor, although we prefer to think of flavor as the combination of the perception of taste in the mouth and retronasal aroma in the nose (see section 2.6 below). It is one of the challenges for Molecular Gastronomy to develop an appropriate language that can be used by chefs, the general public, as well as the scientific community to describe the various ways we interpret the signals from our chemical senses.

When eating a food the initial olfactory stimulation takes place as we smell the aroma of the food before the food is in the mouth. Thus, orthonasal perception is often said to be of the external world. In contrast, the aromas perceived retronasally are said to be of the oral cavity (the interior world).

Small and colleagues³⁵ compared these two distinct pathways of delivering odorants and found different patterns of neural activation depending on whether the aroma compounds are delivered ortho- or retronasally. Further, a few experiments examined differences in perception of aromas delivered by the two pathways; these have rather variable results. In one study, Aubry and colleagues³⁶ found no overall difference in the ability of trained sensory panelists to describe a set of Burgundy wines. By contrast, other research examining the dose–response behavior of flavor molecules ortho- and retronasally have revealed differences which depend strongly on the physical characteristics of the aroma compounds.³⁷ Much further work is needed before we will be able to understand the extent to which individuals perceive odor differently depending on whether they are

delivered ortho- or retronasally; at this stage, all we can do is to note that it is likely that there will be a range of where the initial smell (the orthonasal stimulus) may be rather different from their “flavor” (the combination of the taste and retronasal stimulus). One such example that is well known to gourmets is that of the pungent smelling Durian fruit, which has, for most people, a very unpleasant (toilet-like) aroma when smelled orthonasally but, for many, a very pleasing flavor when in the mouth and the aroma is detected retronasally.

2.3. Chemesthesis

As we have already noted, the overall “flavor” of a food is determined by the combination of many stimuli both in the mouth and nose. Most authors argue the important senses are those of taste, (retronasal) smell, as well as the less well-known, mouthfeel and chemesthesis.³⁸ In this section we will briefly review the sense of chemesthesis.

In humans, sensory nerve endings from branches of the trigeminal nerve are found in the epithelia of the nose and oral cavity. Signals transmitted by these nerves are responsible for the pungency of foods, as exemplified in carbonated drinks, chili, ginger, mustard, and horseradish; accordingly, chemesthesis is also sometimes referred to as the “trigeminal sense”. Hot spices are typical stimulants of trigeminal sensory nerve endings, but most chemicals will stimulate these nerve endings at sufficiently high physical concentration.

Without pungency many foods would be bland; imagine horseradish without the heat or garlic with no bite. Clearly, the sense of chemesthesis must play a crucial role in our the evaluation of the palatability of any food. The sensation of oral pungency differs in many ways from the sense of taste. For example, pungency typically has a slow onset but can persist for prolonged periods, minutes to tens of minutes. This is contrary to the sense of taste, which is most intense for the few seconds the food is in the mouth. This difference in the temporal nature of pungency and taste is of great interest when considering of the palatability of foods and the overall satiety they provide. In many cases, the long-term effects of pungency will make foods both more palatable and more satiating.

Further, the interesting temporal properties of trigeminal sensation may be exploited in the development of new gastronomic meals both for their ability to surprise on a short time scale (seconds) and for reasons of novelty. In the search of “flavor principles”, i.e., rules of thumb of which sensory attributes should be present in a good flavor, trigeminal stimulation certainly will play a large role.

2.4. Texture (Sense of Touch)

Szczesniak³⁹ succinctly defines of texture as “...the sensory and functional manifestation of the structural, mechanical and surface properties of foods detected through the senses of vision, hearing, touch and kinesthetics”. This definition clearly conveys the important point that texture is a sensory property and thus requires a perceiver. The distinction between texture and structure is sometimes ignored in the terminological practice, such that sensory and instrumental measurements can be confused. It is not touch alone that provides the sensation of the texture of food: vision is active in texture perception when we see the food; additionally, audition, somesthesia, and kinesthesia are active during handling of the food. During consumption, the oral process-

ing, the latter three remain active.⁴⁰ Texture plays a major role in our recognition of foods. For example, when presented with blended food products 56 blindfolded young and elderly subjects were, on average, only able to correctly identify 40% of these foods.⁴¹ Our sensitivity to texture under laboratory conditions is very high. The perception of particles in a solution is so sensitive that particles need to be smaller than 3 μm to escape detection. This has been exploited commercially in a number of fat replacers and mimetics (e.g., Simplese, Litesse, LITA, Trailblazer, Stellar⁴²) where spherical microparticulates in the range 0.1–3 μm are the main functional ingredient. When particles are this small they are perceived as smooth and may contribute to creaminess. It has been suggested that the functionality of such small particles is that they rotate relative to each other under shearing conditions present in the mouth, providing a fluidity of the mass of particles with a ‘ball-bearing’ effect.⁴³

Further, there is a marked difference between the food that enters the mouth and the wetted bolus that is later swallowed, and it is the summation of sensory impressions during the whole process from seeing the food, picking it up and putting it our mouths, chewing it, and eventually swallowing it that we perceive as the texture of the food. This has been termed the “philosophy of the breakdown path”.⁴⁴ In this view, individual foods follow specific paths during oral handling along the axes “degree of structure”, “degree of lubrication” over time, or number of chews. Foods interact with the eater during consumption, the saliva lubricates the food, and enzymes in the saliva affect the viscosity of semisolids and liquids. For example, addition or inhibition of α -amylase in a semisolid food affects a number of different sensory properties, among them the highly desirable creaminess.⁴⁵ Finally, we note that astringency is a sensory property that is suggested to result from interaction between proline-rich proteins (PRPs) and polyphenols in the foods. PRPs precipitate polyphenols, causing flocculation and loss of lubrication.⁴⁶

2.5. Temperature

From cold ice cream on a hot summer day to hot cocoa after a trip on the skating rink in winter time, temperature is part of our perception of foods. We have expectations for the serving temperature for most foods and beverages; an inappropriate serving temperatures leads to reduced liking or even rejection of such foods and beverages.⁴⁷ We sense the temperature of food in our mouth through nerve endings. Thermal information appears to be coded primarily by activation of ion channels that belong to the transient receptor potential family.^{48,49} There are six different thermosensitive ion channels. They have distinct thermal activation thresholds (>43 °C for TRPV1, >52 °C for TRPV2, \sim 34–38 °C for TRPV3, \sim 27–35 °C for TRPV4, \sim 25–28 °C for TRPM8, and <17 °C for TRPA1) and are expressed in primary sensory neurons as well as in other tissues. Temperatures above 43 °C and below 15 °C are accompanied by a feeling of pain. However, we routinely consume hot beverages well above both pain and tissue damaging temperatures. A study of ingestive behavior of hot coffee coupled with measures of temperatures during sipping and in mouth showed that minimal cooling occurred during sipping and ingestion. The authors hypothesize that during drinking, the hot coffee is not held in the mouth for a sufficiently long time to heat the epithelial surfaces sufficiently to cause pain or tissue damage.⁵⁰

The perception of temperature changes in the mouth is very precise; under experimental conditions sensitive subjects feel changes in temperature of as little as around 1 °C.⁵¹ The ability to sense changes is asymmetric: increases in temperature are sensed much more rapidly than decreases.⁵² The sensation of temperature can be affected by various chemesthetic agents, with menthol as a well-known example of cooling and capsaicin for heating.

The temperature of a food or beverage affects the release of airborne molecules, with an increase in temperature leading to increased release. For this reason standards in sensory evaluation recommend specific temperatures for products, e.g., milk and other liquid dairy products should be served at 14 ± 2 °C,⁵³ although this is higher than the common consumption temperature.

2.6. Concept of Flavor

Food provides a multimodal stimulus; it excites more than one sensory system. During the process of eating, all of the five senses are used. With our far senses vision and olfaction we see and smell foods from a distance. With our near senses somatosensation and gustation we feel and taste the food during handling and oral processing. In many cases foods elicit our auditory system as they emit sounds during chewing and other oral processing. We use the term flavor to describe our perception of a food, generally thinking of the senses of only taste and aroma. However, in a scientific context, flavor may be defined as “the complex combination of the olfactory, gustatory and trigeminal sensations perceived during tasting. The flavors may be influenced by tactile, thermal, painful and/or kinaesthetic effects and expectations from visual presentation of the product”. Since flavor is a multimodal sensory experience it has been difficult to relate the concept of flavor with the chemical components of foods.

2.7. Multimodal Integration

In foods there are several examples where the perception in one sense interacts with that of another sense. The taste of a food may be affected by changes in the texture. It has been demonstrated repeatedly that this is a perceptual phenomena, as a harder texture of a gel decreases the perceived intensity but hardly affects the release of aroma compounds, as measured by the concentration in the nasal cavity.^{54,55} Aroma compounds in a food can also enhance perceived taste intensity of congruent tastes, e.g., the intensity of sweetness in whipped cream can be increased by adding strawberry flavor but not by adding a peanut butter flavor.⁵⁶ Frank and Byram⁵⁶ also showed that the effect can be eliminated by pinching the nostrils during tasting. The taste-enhancing properties of an aroma depend on conditioning through repeated pairing of an aroma with a taste. This learning occurs very fast and implicitly during few exposures. Completely novel odors paired with tastants take on the tastants’ properties (sweet or sour) with only one exposure.⁵⁷ The past decade has seen an explosion in research in the field of multisensory integration. Much of this stems from advances in neuroscience, and recently, interest has expanded from integration in vision, audition, and somatosensation to also encompassing the chemical senses. A very thorough review of the field of human multimodal food perception was performed by Verhagen and Engelen⁵⁸ and includes some plausible neuroscientific models and suggestions for future research. Some specific sensory properties are of a

more complex nature than others, and these involve more than one sense. A commercially important property in this category is creaminess, originally suggested to be a texture property only. It has been researched intensively in the past decade, and the research suggests that although texture may be most decisive for creaminess, its perception involves several senses, at least including vision, olfaction, gustation, and haptics.^{59,60}

2.8. Adaptation and Suppression

In addition to the actual signals from the sensors, there are further, perhaps surprising ways in which we perceive the environment around us which can significantly affect the flavor of the food we are eating. Two of the most important are adaptation, when we ignore a constant stimulus, and suppression, when we find the effect of a stimulus in a mixture less than on its own. Both are of some significance in the kitchen, so we will describe them in more detail below.

2.8.1. Adaptation

When subject to a constant stimulus, the senses become less responsive. When holding a solution of a tastant (e.g., sucrose) motionless in the mouth, the solution will become completely tasteless after a while.⁶¹

This phenomenon is well known to us all, although we tend to ignore it. Whenever we leave our homes for a prolonged period, to go on holiday or to a week-long conference, we find on our return that as soon as we walk in the front door our home has a slightly “musty” smell. Thus, we open the windows and “air” the house. The odor quickly goes away. Of course, in actual fact, our homes always have that smell, it is what our friends and neighbors perceive as the smell of our home. However, because it is always present in our environment we rapidly become adapted to it and simply do not notice it at all. When eating, we will quickly become “bored” with a dish which appears to lose its flavor if we are subject to the same taste or aroma continuously for a prolonged period. Variety becomes the spice of life.

If we are aware of this phenomenon we can make all meals more interesting simply by increasing variety, a large number of small differently flavored or textured dishes (such as the Spanish Tapas) will provide greater interest than one single, larger item. Many restaurants provide a diverse range of elements on every plate; some very small items can break up a larger item to provide the necessary changing stimulus to retain the diner’s interest and enjoyment.

In the gastronomic kitchen, some chefs, having recognized the adaptation phenomenon, have tried to create dishes that continually provide a diverse range of stimuli so as to retain (and hopefully enhance) the diner’s interest. One such example comes from the Fat Duck, cauliflower risotto.⁶² The central idea here was to take a vegetable, regarded by many as essentially rather uninteresting (i.e., one that in which diners might quickly lose interest as they start to ignore the flavor), but to prepare a dish that has a wide variety of different textures and flavors that constantly stimulate the brain, so preventing any adaptation and (hopefully) turning a plain cauliflower into a very tasty and exciting dish. The result was “cauliflower risotto” (for a photograph see page 323 of *The Big Fat Duck Cookbook*⁶²) a dish that was for some time one of the signature dishes at the Fat Duck.

To achieve the desired effect, Heston Blumenthal used a combination of many different cauliflower preparations (dried cauliflower, cauliflower cream, foamed cauliflower, raw cauliflower, and a risotto made with a cauliflower stock together with other contrasting ingredients such as cocoa jellies) to create a spectacular dish of which no diner is likely to tire.

2.8.2. Mixture Suppression

Mixture suppression is the phenomenon that individual taste and smell characteristics are perceived as less intense in mixtures than alone.⁶³ Thus, when preparing a complex recipe and mixing several foods with different flavors or tastes, the perceived intensity of the flavors of the separate ingredients is decreased relative to that of the same tastes or aromas of the ingredients on their own. There is a very interesting and useful exception to this phenomenon, *Release from suppression*; when adapting to one component in a mixture, other components are less suppressed and will then be perceived as more intense.⁶⁴ This is routinely used by flavorists and perfumers to analyze competitors’ blends.⁶⁵

Once again, awareness of the issue can quickly provide new ideas to improve cooking. Rather than mixing all the ingredients together in a single pot, it can be much better to present them separately. For example, there may be several different sauces or dips associated with a single dish; if these are presented in separate pots and used individually, rather than in combination, their impact is greater.

3. How Different Food Production Techniques May Affect Flavor and Texture

The first stage of the preparation of any meal is the production of the basic ingredients, something which normally is out of the control of the cook and happens well before any processing of the food begins. In this section we briefly address the question of whether science can help us understand the extent to which the selection of particular ingredients according to the ways in which they are produced actually affects the flavor of a completed dish.

It is often said that the finest food requires the best ingredients. However, how can we begin to define what makes the “best” ingredients? How can we tell whether one carrot is better than another? Of course, there are no specific answers to such questions; not only will there be an element of personal preference as to which carrot is better, but one carrot may be better suited to eating raw in a salad and another to being cooked in a casserole.

Most cooks and chefs hold strong views on what is best; many insist that one particular production technique (such as organic farming) consistently yields better produce; others may insist the key factor is the “freshness” of the ingredients. Unfortunately, as we will see, there is little clear scientific evidence to back up such assertions and what literature that does exist is often vague and contradictory.

However, there are a few cases where the effect of the production, storage, and even transport on foodstuffs has been well investigated and some understanding of the effect on flavor has been achieved. In particular, it is now well established that the flavor of meat is affected by the food eaten by the animals it is produced from, that the flavor and color of dairy products depends on the forage of the animals used to produce the milk, that the flavor of fruit and vegetables is influenced strongly by the variety used, and

that growing conditions affect volatile compounds and hence flavor in many vegetables. The way in which animals are slaughtered and the subsequent storage of the meat is also known to affect not only the flavor but also the texture of the final product.

In this section we briefly look at what is known about the extent to which the production methods of food affect the ultimate quality to see how far this knowledge can actually be applied in practice in the kitchen.

3.1. Organic vs Conventional Farming

Most people, if asked, will assume that organic foods taste better than those grown conventionally. However, there is little, if any, real evidence to bear this out. In a comprehensive review of the literature on the nutritional value, sensory quality, and food safety of organically and conventionally produced foods with emphasis on the comparison between organic and conventional growing methods for fruit and vegetables Bourn and Prescott⁶⁶ clearly showed that the results from a large number of studies are not only inconclusive but also mutually contradictory. Further, they demonstrated that the scientific methods in many of these studies were questionable with the effects sought after widely being confounded with other factors.

Bourn and Prescott, in common with an earlier review by Woese et al.,⁶⁷ note that there was a tendency for some organically grown foods to contain a smaller amount of nitrate than conventionally grown vegetables, probably, they suggest, due to greater quantities of nitrogen being used in conventional farming. However, they also note that it remains to be seen whether this is a general effect across a wide range of organic produce. Whether the nitrate content significantly affects taste (and whether any such effects are positive or negative) is not known; this might prove a fruitful area for future research. In a separate survey of the literature, Williams⁶⁸ reached similar conclusions but also noted that vitamin C had been found to be at higher levels in organically grown vegetables than in conventionally grown ones. Zhao et al.⁶⁹ found consumers could not tell any difference between the taste and the flavor of organically and conventionally grown vegetables, even though 28% of the consumers had expected organically grown vegetables to taste better than those grown conventionally.

3.2. Effect of Feed on the Flavor of Meat

Common experience, backed up by a number of detailed scientific studies, leaves no doubt that how animals are fed influences the flavor of the meat. However, whether the influence of the feed is to produce “better” flavors is not so clear.

Several studies have shown that the composition of the fatty acids found in the fat tissue of the animal reflects the composition of fatty acids in the lipids fed to the animal. If the animal is fed a diet containing unsaturated fat, then the fat tissue in the animal will contain a larger degree of unsaturated fat than animals fed a normal diet.^{70,71} Decreases in saturated fats may have health advantages; for example, in one study it was shown that when people eat meat from pigs fed on a diet with added rapeseed oil their cholesterol levels were reduced when compared to a group that ate meat from pigs fed a normal diet.⁷² However, since unsaturated fats generally melt at lower temperatures they are more likely to be lost in cooking, leading to potentially drier textures.

Importantly, changes in the proportion of saturated fats lead to noticeable changes in meat flavor. Meat with a higher proportion of saturated fat usually has the preferred flavor, although this may simply be an affect of liking that to which we have become accustomed. Perceived changes in flavor with differences in fat saturation are most pronounced in lamb and beef and much less noticeable in pork.⁷⁰

Studies have been performed comparing the flavor of pork, lamb, beef, poultry, red deer, and reindeer with different feed sources for the animals. The main conclusion from these studies is that what the animal eats will be reflected in the flavor of the meat.^{70,73–76} High-energy grain diets produce a more acceptable or intense flavor in red meat. Other dietary ingredients such as fish products, raw soybeans, and pasture grasses can have an undesired effect on meat flavor. Some researchers have even tried feeding horse manure and spoiled meat scraps to pigs, which, not surprisingly, resulted in foul smelling meat with the undesired flavor located in the lean muscle tissue.⁷⁰ Meat with a higher proportion of unsaturated fat usually has more tendency to develop off flavors during cooking as a result of lipid oxidation, see section 4.1.2.3.

It is however worth noting that there is no single “beef” (or lamb, or pork) flavor; rather there is a wide range of flavors that can be achieved depending on the way in which the meat has been produced (and later cooked). In practice, the good chef will try out meats from a wide range of different sources and select that which best suits his particular purpose in any dish, but he would be well advised to ask the butcher for details of the production methods so that he can be sure, in the future, that he will be able to obtain, as nearly as possible, an identical product.


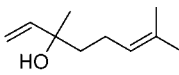
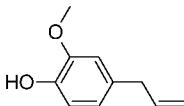
3.3. Effect of Feed on the Flavor and Texture of Dairy Products

The color and flavor of dairy products are influenced by the forage. Diets high in grass (as grass silage or fresh pasture) give products that are more yellow, whereas diets rich in maize silage yield very white products. The yellow color is due to β -carotene from the forage.⁷⁷ Since β -carotene is degraded during hay production,⁷⁷ feeding hay to the cows does not have the same effect on the color as pasture. In Northern countries where cattle are generally kept indoors and fed on hay, winter cheeses and butter made from winter milk are whiter than products made from summer milk, when the cows have been on pasture.^{77,78}

The different plant species that grow at high and low altitudes lead to different volatiles in the milk of cows reared at different heights, leading to significant differences in the flavor of “mountain” and “valley” cheeses, especially those from Switzerland.⁷⁷

The texture of dairy products is mainly influenced by a differing degree of saturation of the fat. Increasing the content of unsaturated fat leads to a softer product in, for example, cheese and butter. Cows on pasture will produce milk with more unsaturated fats than cows fed preserved forage.⁷⁷ In a study of relationships between chemical and sensory properties of milk from cows fed on different forages, it was shown that milk with a high content of long-chain saturated fatty acids produced milks with high levels of lipolysis, leading to flavors characterized as Roquefort.⁷⁹ Subsequent studies have shown that more subtle differences in composition stemming from differences in feed provide recognizable differences in sensory properties.^{80,81}

Table 1. Content of Selected Odor Components in Basil (ppm) As Influenced by Growth Temperature^a

Temperature (°C)	Odor Compound		
			
	1,8 Cineole	Linalool	Eugenol
15	15.0	15.4	2.9
25	25.0	29.6	4.5

^a Eugenol contributes to the characteristic taste of basil. Adapted from Chang et al.⁸⁶

It is worth noting here that fresh dairy products (milk, cream, etc.) will have properties that depend on local conditions, so that the texture, color and flavor of milk will depend not only on locality but also on the time of year and even on recent climatic conditions. Accordingly, cooks need to be aware that they will, from time to time, have to adapt recipes to allow for such variations.

3.4. Flavor Variation in Fruits and Vegetables

Of course, the flavor of plants depends on many factors, not the least of which is the actual variety of the species being grown. Perhaps the best example comes from the world of wine, where different grape varieties or grapes of the same variety grown in different places impart quite distinct flavor characteristics. It is perhaps less well understood that similar variations occur in more or less all fruits and vegetables. For example, in a study of 89 elderflower varieties Kaack et al.⁸² have shown large variations in the concentration of flavor components between different elderflower varieties. Similar studies illustrate that the flavor of tomatoes depends strongly on the variety.⁸³ This means that it is essential to choose the right variety for the right purpose and that the variety can have a large impact on achieving the desired balance between fruity, spicy, floral, fresh, and sweet flavors.

In one particularly detailed study (of 28 Apricot varieties) Aubert and Chanforan⁸⁴ found they could divide the varieties into four groups according to their relative concentrations of 33 volatile components. Group I was characterized by a high content of terpenic compounds (which tend to give a citrus aroma), group II by a high proportion of lactones (coconut and peachy aroma), group III by a high content of esters (with their generally fruity notes) and a low content of terpenes, and group IV by a high proportion of esters.

As well as the variety growth conditions, nutrients and minerals in the soil as well as temperature and general climatic conditions all affect the final flavor. For example, Chang et al.⁸⁵ have shown that the volatile oil content of basil differs according to the growth temperature. Plants grown at higher temperatures (25 °C rather than 15 °C) had significantly larger contents of volatile oils, eugenol, linalool, and 1,8-cineole, as illustrated in Table 1.

How fruits and vegetables are treated after harvest also has a large impact on their eating quality. Tomatoes are often stored under reduced levels of oxygen at temperatures below ambient temperature. One study showed that storage at 6 °C or in low-oxygen atmosphere significantly decreased the concentration of several volatile components. In plain language, tomatoes lose their flavor under normal storage conditions.⁸⁷

If stored at ambient temperature rather than being cooled, in the short term most of the volatile components increase in concentration during the 10 days postharvest period. This is however a double-edged sword as in sensory tests the tomatoes not only scored higher in tomato-like flavors (desired) but also in moldy flavors (undesired).⁸³ In a different study Boukobza and Taylor⁸⁷ also showed an increase in volatile components in tomatoes during storage at ambient temperature in an unaltered atmosphere.

Carrots also show quite significant changes in flavor on storage with quite different effects depending on the temperature at which they are stored. Refrigerated storage of carrots for up to 4 months increases the concentration of terpenoids significantly more than frozen storage. An increase in volatile terpenes gives a more “carrot-like” flavor up to a certain concentration, beyond which they cause an undesirable harsh and burning flavor.⁸⁸

4. Food Processing (Cookery)

Of course, it is only with the preparation of the raw ingredients in the kitchen and then combining them and cooking them in the appropriate manner that the true quality of a plate of food is developed. All this can involve many separate processes; some develop flavor, others develop textures, and many affect both. This is the largest section of the review and is divided, largely, into processes that create and develop flavor and those that are more aimed at modifying and creating specific textures.

We have deliberately chosen to consider mainly the processes of small-scale (domestic and restaurant) cooking. However, we will not limit ourselves to processes that are currently used in a domestic environment. Already some techniques from the science laboratory are finding their way into restaurant kitchens; for example, the use of ultrasonic agitation to create emulsions, the use of liquid nitrogen to freeze without allowing the formation of large ice crystals, the use of well-controlled temperature baths for poaching, and the use of vacuum desiccators to remove water from potatoes before roasting; these techniques could soon arrive in our own domestic kitchens.

We begin by looking at how flavor is developed through chemical reactions that produce new volatile “aroma” molecules and then move on to look at how color and texture are developed in the kitchen and examine how the textures affect the flavor, for example, by modifying the rate or order of release of different aroma molecules in a given food.

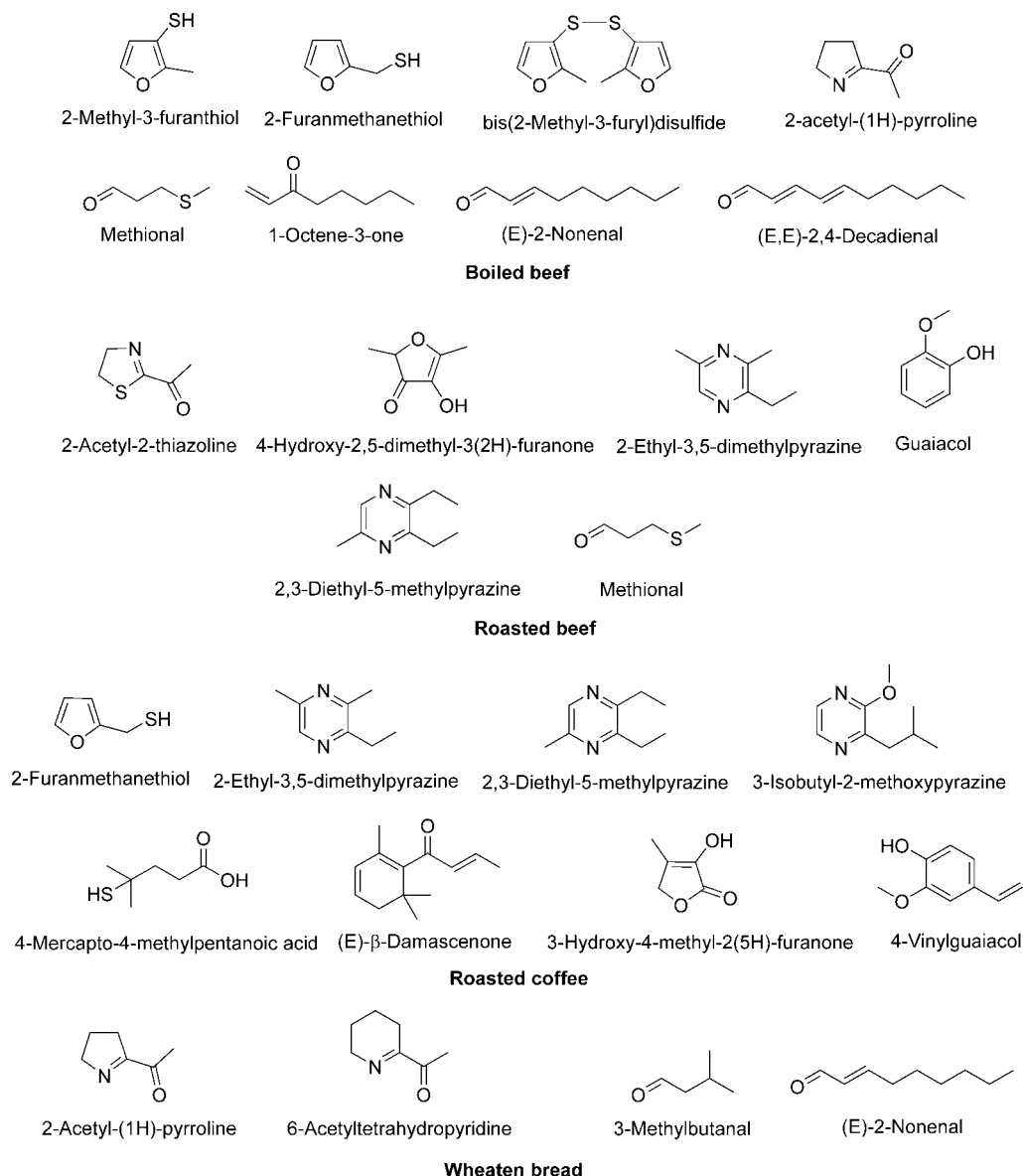


Figure 2. Aroma impact compounds in heated foods as identified by the AEDA technique.⁸⁹

4.1. Flavor Development

To a food chemist, flavor is determined from an analysis of the aroma and nonvolatile molecules present in a foodstuff. It is possible to group volatile molecules by the sort of aromatic notes they provide (meat, fruit, bitter, nutty, etc.) and in some cases to be even more specific. Using aroma extract dilution analysis (AEDA) Grosch and co-workers succeeded in identifying key aroma impact compounds in a range of foods.⁸⁹ An example is given in Figure 2 for foods that have undergone a thermal treatment and in Figure 3 for nonheated foods.⁸⁹ Even though the TNO collection of volatile compounds in foods (VCF) reports over 10 400 entries,⁹⁰ only a very few of these compounds actually contribute to the key flavor notes in foods.

Accordingly, much effort has gone into trying to understand the chemical reactions that produce these volatile aroma molecules. Table 2 puts together an example of some important low odor threshold odorants encountered in heated and typical foods. Chefs, by contrast, have an empirical understanding of flavor based on experience and an intuitive understanding of how flavor develops as the cooking progresses, backed up by the continual tasting of everything

they prepare. The scientific approach has the advantage that it should be objective and can, in principle, provide instructions that give reasonably reproducible results despite the variability in ingredients. A major problem is that we do not have any way of scientifically describing the nuances of flavor, so the empirical approach of the cook, while it cannot, as yet, be quantified, generally leads to the better result.

However, cooks often tend slavishly to follow a known and practised route to achieve their desired goals, but with a little basic understanding of the key chemical reactions and the conditions under which they produce the different types of aroma molecules there is at least the possibility that the chef can try out and develop with success new ways to achieve his desired final flavor (and even perhaps discover along the way different flavors that might entice the diner).

4.1.1. Microbial Reactions

Microbial reactions due to yeasts and bacteria have been essential to the development of our whole cuisine. Historically the yeasts that cause alcoholic fermentations have been used to make some of the most important staples of our diet, especially breads, beers, and wines. The main reaction of

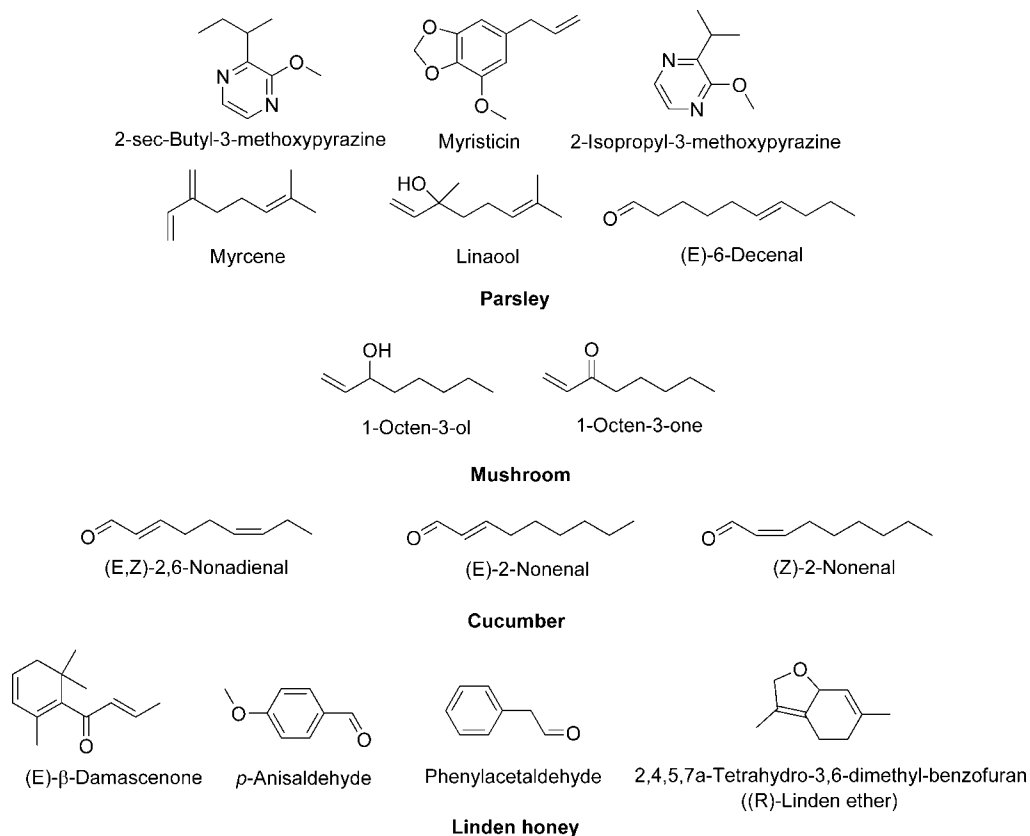


Figure 3. Aroma impact compounds in some nonheated foods as identified by the AEDA technique.⁸⁹

Table 2. Some Examples of Odorants Found in Foods and Their Aromas from Data in Food Chemistry⁹¹

chemical	aroma description	odor threshold ($\mu\text{g/L}$ water)	some examples where it is found
Ethanal	sharp, fruity, sweet	15	Strecker reaction
Methyl propanal	malty	0.7	Strecker reaction
2-Phenylethanal	honey	4	Strecker reaction
4-Hydroxy-2,5 dimethylfuranone (furanol)	heat-treated strawberries, pineapple	ca. 1	beer, bread, pineapples, strawberries
2-Acetylthiazole	popcorn	10	fried foods
2-Isobutylthiazole	green tomatoes	3	fried foods
2-Acetyl-(1H)-pyrroline	white bread crust	0.1	popcorn
3-Ethyl-3-methylpyrazine	burnt flavor	130	roasted peanuts
2-Isobutyl-3-methoxypyrazine	potatoes	0.002	potato products
2-Isobutyl-3-methoxypyrazine	red peppers	0.002	paprika
2-Ethyl-3,6-dimethylpyrazine	hazelnuts	20	glucose syrup
2-Methoxy-4-vinylphenol	cloves	5	coffee, beer, asparagus
4-Methoxy-2-methyl-2-butanethiol	blackcurrants	0.000002	olive oils

the fermentation⁹² process is to convert sugars, including short-chain carbohydrates, to yield carbon dioxide gas, which makes bread rise and gives beer its fizz, and ethanol, which adds flavor and preserves beers and wines as well as providing them with an active effect on the consumer. However, there are many additional side reactions that produce other volatile compounds.⁹³⁻⁹⁵ It is these compounds that impart the distinctive, and appealing, flavors to the various cheeses, breads, beers, and wines with which we have become familiar over the centuries.

Initially all these fermentation reactions were produced using wild yeasts carried in the air, on the skins of fruits, or on seed cases of the grains. Not only did this make the processes somewhat hit and miss, it also led to great variability in both the flavor and the quality of the resulting products. Today most manufacturers rely on cultured yeasts to provide consistent products. Those who have tried to make beer at home will almost certainly at some time have encountered the problem that some batches simply do not

have the same flavor as others and occasionally are quite undrinkable. While some wild yeasts do make pleasant beers, it is generally best to stick to one of the specially cultured yeasts designed over the years to produce high-quality beers such as *S. carlsbergensis*.

There is another slightly different fermentation process that occurs when lactic acid bacteria (e.g., *Oenococcus oeni*) convert malic to lactic acid;⁹⁶ this is known as malolactic fermentation. In wine making the malolactic fermentation can be particularly advantageous since lactic acid has a softer, rounder taste than malic acid, which is perceived as rather "tart". Thus, wines that have undergone malolactic conversion tend to appear softer, have a more rounded mouth feel and have a buttery note that comes from diacetyl produced during the malolactic fermentation.^{97,98} Conversely, since malic acid has the taste of apples, wines that have not been subject to malolactic conversion tend to have a green apple note.

Malolactic fermentation sometimes occurs unintentionally after the wine is bottled. The result is a slightly carbonated wine that usually tastes bad as the wild bacteria that can cause the malolactic fermentation produce a wide range of “off flavors”. Accordingly, many wine makers tend to inoculate their wines in the vats with a culture of desirable bacteria to avoid any risk of accidental malolactic fermentation in the bottle and thus prevent the possibility of any such off flavors occurring.

Of course, by far the largest application of bacteria that produce lactic acid is in the fermentation of dairy products to produce yogurts, soured creams, acidified milks, and of course cheeses. In general, the bacteria convert lactose in milk to lactic acid, thus decreasing the pH of the milk and causing it to aggregate. Different bacterial strains follow somewhat different routes and can produce a range of side products, including diacetyl (giving a buttery taste), acetaldehyde (characteristic of yogurts), as well as carbon dioxide and ethanol. Some Swiss cheeses owe their characteristic holes to the use of carbon dioxide producing bacteria.

As with the use of fermentation to produce breads, beers, and wines, much of the fermentation of dairy products relied initially on strains of wild bacteria which were generally cultivated in local and domestic production by the simple process of adding a little of the previous batch to the next one to be made (backslopping). Today, with the centralization of production of most dairy products many of these individual strains have been lost along with their unique flavors. This perhaps accounts for the increasing popularity of small “boutique” producers who continue to use more traditional methods and thus provide a range of different and distinctive flavors in their products.

The flavor of fermented dairy products comes from a wide variety of molecules which can be formed during reactions. However, in most of the fermentation processes a range of small oxo compounds are produced. For example, in butter production the difference between sweet butter and acidified butter is the presence of diacetyl resulting from fermentation.^{93,95,98} Sweet butters are often preferred for certain dishes due to the milder flavor. Another example is that yogurt often develops a rather tart flavor due to the production of acetaldehyde. This is often disguised in fruit yogurts by the addition of sugars, causing the sweet flavor to become dominant.

A similar process has occurred with a range of meat products. In Southern Europe sausages were often fermented with added spices and then air dried to yield specific flavors and good long-term storage properties. In Northern Europe smoke was more often used to dry the sausages giving other flavors while also imparting excellent preservative characteristics. In the intermediate regions such as Hungary fermented sausages were matured for longer times at lower temperatures and covered by molds to help preserve them. Once again, modern centralized production is inevitably leading to the loss of some of the bacterial strains used in these traditional processes and with that the potential loss of some unique flavors.

4.1.2. Chemical Reactions Affecting Flavor

While raw ingredients carry with them a vast array of naturally occurring flavors, think of fragrant strawberries, sweet carrots, mildly acidic apples, and sharp limes, many of our most favored flavors today actually do not occur directly in nature but are created through chemical reactions

within and between the food ingredients after harvesting. Without chemistry there would be no chocolate, no coffee, and no “meaty” flavors. There are so many different chemical reactions that go into generating these flavors, and they differ subtly in every kitchen with slightly different ingredients, temperatures, and tools, making it quite impossible to list them all.

Instead, in this section we will simply attempt to extract from the vast literature some of the more salient issues of flavor development from the wide variety of chemical reactions that occur as we prepare our foods. Some of these occur before we start any cooking; they happen either in the mouth as enzymes in saliva react with molecules in the raw ingredients or when the raw ingredients are cut open, bringing enzymes into contact with the substrates upon which they can act. We briefly discuss such reactions in the first part of this section.

In the remainder of the section we briefly review a range of different types of chemical reactions that break larger molecules into small volatile compounds that can (and do) greatly affect the flavor of our foods when we process them further (usually under the influence of heat). These include hydrolysis, oxidation, and the Maillard and caramelization reactions, each of which is discussed separately even though in real cookery all can (and do) occur simultaneously.

4.1.2.1. Physical Processing. The first stage of processing of most fresh ingredients involves cutting or otherwise breaking them into smaller pieces. In many cases the very fact of fracturing the cell walls leads immediately to the release of enzymes and the start of enzymatic reactions that alter the flavor.

In many plants enzymes are separated from their substrate so as to avoid reactions occurring when the plant is growing. However, when the cellular structure is destroyed by, for example, cutting or grinding by the cook or chewing by the diner they come into contact and flavor-producing reactions may occur.

The pungent taste of several plants in the *Cruciferae* (*Brassicaceae*) family, including, for example, mustard, horseradish, and wasabi, occurs via breakdown products from glucosinolates. The glucosinolates are hydrolyzed to isothiocyanates when the enzyme myrosinase (thioglucoside glucohydrolase) is released due to plant tissue being mechanically disrupted or injured by, for example, chewing/crushing/grating.^{99–103}

A similar process in *Allium* species such as onions, leek, and garlic provides the characteristic flavor formed when plant tissue is disrupted, releasing alliinase. The enzyme released in this process breaks down odorless sulfur-containing amino acids (*S*-alk(en)-yl-L-cysteines) and their sulfoxides. These are cleaved to yield pyruvate, ammonia, and sulfur-containing volatiles (Figure 4), giving the characteristic pungency and lachrymatory effect.^{104–109}

It is important to note that thermal processing of the vegetables denatures the enzymes responsible for these reactions;^{102,111} hence, preparing, for example, onions and garlic whole in the oven gives a much milder and rather different flavor since the enzyme will never become active. The alliinase can be inactivated irreversibly at low pH (below 3), preventing these reactions to occur. Thus, acid marinating directly after cutting and crushing would result in similar mild flavors.

4.1.2.2. Hydrolysis. Many of the nutritionally important molecules in our food are large polymers, e.g., starches and proteins; these are neither particularly soluble or volatile and

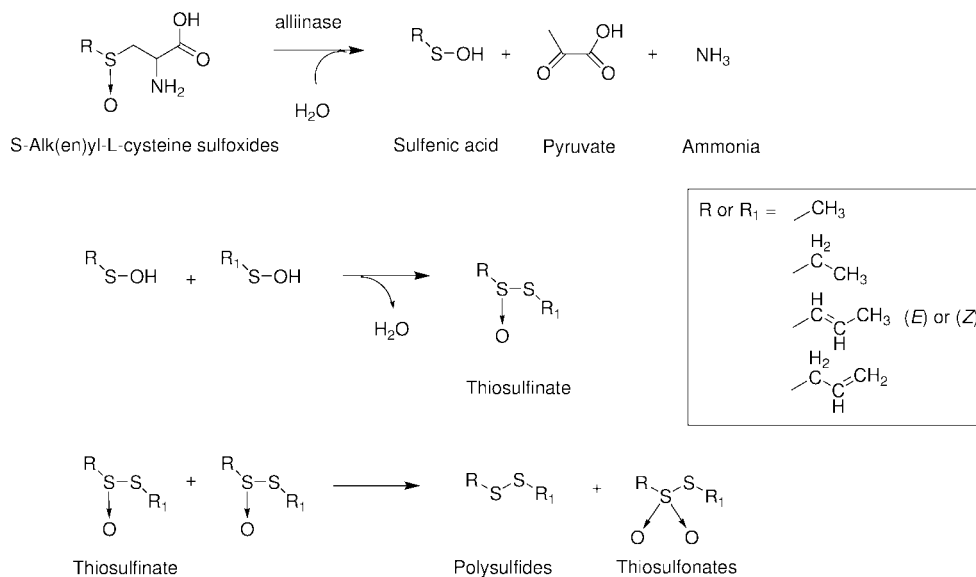


Figure 4. Formation of potent sulfur-containing compounds in *Allium* species.¹¹⁰

so have little if any perceivable taste or aroma. We can only detect their presence in foods though the textures they create and not by any specific taste. However, when degraded into smaller molecules they generate a wide range of tastants and aromatics that we can and do enjoy in the taste and smell of our foods. While there are several different routes through which such degradation can occur, hydrolysis is probably the most important of these and the subject of this section.

The three macronutrients carbohydrate, proteins, and lipids are all able to react with water so that the macromolecules are degraded into smaller pieces which are likely to possess aroma or flavor (which may be pleasant or in some cases unpleasant). Carbohydrates are polymers in which the monomers (sugars) are linked together by glycosidic bonds, which may hydrolyze as a result of acid catalysis or via enzymatic reactions. For example, malting, the initial stage in brewing beer, is an enzymatic hydrolysis of starch which produces smaller carbohydrates, making them available for the yeast to convert to alcohol and carbon dioxide. The sweet taste of malted bread is similarly produced from the small carbohydrates or oligosaccharides produced by hydrolysis.

Proteins may, in addition to the enzymatic and acid-catalyzed hydrolysis seen in carbohydrates, also hydrolyze via base catalysis since the amino acids are linked together by amide bonds. For example, proteins can be hydrolyzed during the ripening of cheese or boiling of meats. In this process shorter peptides are formed which eventually can be cleaved to individual amino acids. In general, the more hydrophobic amino acids taste bitter,¹¹² while the more hydrophilic amino acids have a neutral or sweet taste.^{112,113} Thus, peptides with specific combinations of hydrophobic amino acids can be extremely bitter and may ruin the flavor of cheeses if formed in significant quantities. The amino acid glutamic acid (and small peptides with glutamic acid) are often formed during cooking of meat, in soups, and in savory cheeses. These are particularly important as they excite the umami taste sensation, giving these foods their characteristic rounded flavors. Most foodstuffs are either acidic or neutral, so base catalysis is relatively uncommon. However, in fish treated with lime or other alkaline substances (as is traditional in some Scandinavian and Asian countries) hydrolysis through base catalysis plays a significant role in flavor development.

Lipolytic enzymes can hydrolytically cleave the lipids to form free fatty acids; these reactions are particularly important when considering rancidity in oils and fats. For example, olive oil is produced from fruit pulp which has a high lipid content; these lipids are easily hydrolyzed by enzymes so that the oil can contain significant quantities of free fatty acids.¹¹⁴ A high content of free fatty acids in an oil lowers its thermal stability during frying which may impair its flavor. Similarly, butter may go rancid due to lipid hydrolysis of butterfat to produce short-chained fatty acids such as butyric acid, ruining the flavor.

In some sausages lipid hydrolysis during fermentation and ripening actually provides a more soapy flavor, which is not necessarily negative for the overall flavor.¹¹⁵ Partially hydrolyzed lipids are surface active and find use as emulsifiers, for example, in bread to reduce staling and starch crystallization.

Mold ripening of cheese yields very complex flavors. The initial ripening occurs through protein hydrolysis and is followed by lipolysis, while for blue cheeses like Danablu and Roquefort free fatty acids make significant contributions to the flavor.

4.1.2.3. Oxidation. A second process that can degrade food molecules is oxidation. Unlike hydrolysis, in nearly all cases oxidation leads to flavors that are not desirable, so we normally strive to reduce or avoid oxidation during storage and processing of fresh ingredients.

Oxidation of foods may be initiated enzymatically, for example, in vegetables post harvest, by catalysis by transition-metal ions, which can occur, for example, when using copper pans for frying, or by exposure to light, as happens with green plant oils. Most food components are vulnerable to oxidation, and oxidation may change their flavor, color, and nutritive value. In the kitchen we are familiar with oxidation especially in relation to lipids; vegetable oils and lard may go rancid during storage, while pork and poultry often develop a so-called “warmed-over flavor”¹¹⁶ upon reheating. Among the lipids, the degree of unsaturation is crucial. Oils and fats from fish are extremely sensitive to oxidation, while animal fats from ruminants are less sensitive; lard and plant oils have intermediate sensitivity. The propensity to oxidation depends on the degree of unsaturation of the lipids and on the level and nature of any antioxidants

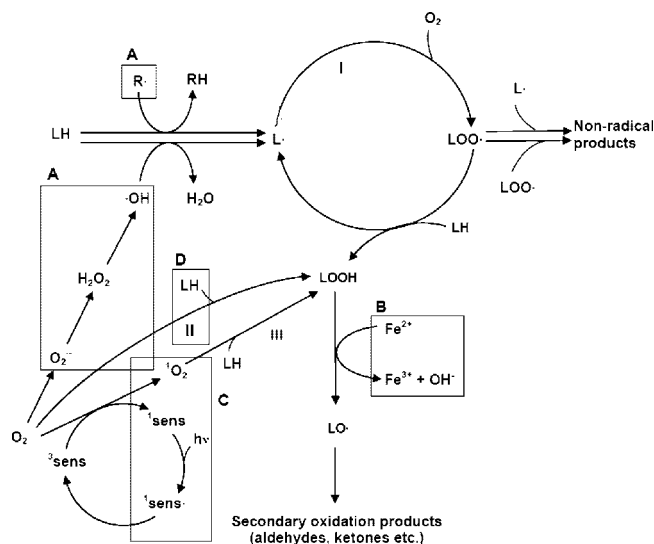


Figure 5. Lipid oxidation may be initiated by free radicals or enzymatically (A), by transition metal catalysis (B), photochemically (C), or by lipoxygenases (D).

present. A convenient illustration can be seen in the best choice of various plant oils for cooking. Heavily unsaturated oils such as pumpkin oil and walnut oil oxidize easily on heating and should never be used for frying, while they are perfect for dressings with their mild and unique taste. More saturated oils such as palm oil, rapeseed oil (canola), and olive oil are almost perfect for frying having high monounsaturated content, while grape-seed oil and soy oil should be used with care due to the increasing amounts of polyunsaturated fatty acids present in the lipids. Olive oil adds a unique flavor to fried vegetables or meat, while canola oil is more neutral and accordingly preferred by some.

The reuse of oil for frying, as is often the case in deep frying, can generate new flavors that are characteristic of the specific oil used; often these flavors can be unpleasant and are classed as “off flavors”. Fatty acids belonging to the Ω -9 family such as oleic acid have the major oxidation product nonanal, while hexanal dominates the oxidation of the Ω -6 fatty acids and propanal the Ω -3 fatty acids. Hexanal has been found to be an important compound in warmed-over flavor.^{116,117}

Another important aspect of oxidation of foods in the kitchen is the oxidative polymerization of polyphenoles which causes the enzymatic browning in avocados and apples. Control of enzymatic browning is also important for producing tea. Green teas are obtained by deactivating polyphenoloxidases by heating freshly picked leaves, black teas get their color from polyphenoloxidase activity, while oolong teas obtain their light brown color by strictly controlled heat deactivation of the enzymes. Notably, co-oxidation of carotenoides in the tea leaves is crucial for the development of the flowery notes characteristics for the fermented tea.

4.1.2.4. Lipid Oxidation and Antioxidants. Lipid oxidation is a chain reaction with free radicals as reactive intermediates.¹¹⁸ Lipid oxidation depends on oxygen activation or attack by free radicals on the lipids, leading to formation of lipid hydroperoxides without flavor as the primary oxidative products as illustrated in Figure 5. Oxygen activation by metal-ion catalysis may produce the hydroxyl radical capable of initiating the chain reaction (A in Figure 5). Lipoxygenase (D in Figure 5) results in direct formation

of the lipid hydroperoxides, and also photosensitization by chlorophylls and other pigments (C in Figure 5) is important. Secondary lipid oxidation products are formed by cleavage of the hydroperoxides to form aldehydes and ketones with low sensory threshold values.

Metal catalysis cleavage of the hydroperoxides may be due to the redox activity of heme pigments. The traditional use of thyme to spice blood sausages in traditional Nordic cooking is an example of the beneficial effect of a natural antioxidant. Thyme prevents any oxidized flavor as phenolic compounds such as thymol and carvacrol present in thyme provide antioxidant protection. Phenolic antioxidants, to which class vitamin E, α -tocopherol, also belongs, are chain breaking as they donate a hydrogen atom to the lipid radical in the reaction marked by A in Figure 5. Another example of a traditional source of natural antioxidants is rosemary; many traditional dishes spiced with rosemary are inherently protected against warmed-over flavor by the phenols from rosemary.¹¹⁹

Interestingly, the lipoxygenase enzymes can be active even at the low temperature of frozen storage.¹²⁰ This is the reason why blanching of vegetables prior to frozen storage to inhibit such lipid oxidation being initiated by lipoxygenase is important (D in Figure 5).

Carotenoids which are present together with the chlorophylls in the photosynthetic apparatus in plant cells yield protection against photo-oxidation¹²¹ (C in Figure 5). Photo-oxidation is a comparatively slow process and seldom a problem in the kitchen. However, changes due to photo-oxidation will occur in some foods when stored in the light. For example, virgin olive oil and other green vegetable oils should never be stored in light as they will slowly oxidize. Thus, even though a bottle of olive oil in the kitchen window can be very decorative it is not a good idea as the oil will slowly deteriorate.

A third antioxidative mechanism depends on the complexation of pro-oxidative metals by flavonoides¹²² (B in Figure 5). Onions, which are rich in quercetin, may be active by this mechanism when added to high-fat fresh sausages and pâtés. Green tea rich in catechin holds the potential for a similar use in other dishes.^{123,124}

The quality of raw material is important for the oxidative stability. For nonruminants the feeding regime is crucial. A large supply of unsaturated lipids in the feed increases the risk of oxidation in the meat, while a rich supply of antioxidants from herbs or other sources such as acorns yields protection. On the Iberian Peninsula pigs for the highly praised dry cured hams finish their lives roaming in the cork oak grooves feeding on acorns rich in antioxidants. Lipid oxidation in such products is characterized by a lag phase, the duration of which depends on the feeding regime. As long as the antioxidants are available at a sufficient level, the lipids are protected, while when they are depleted, oxidation wins and the meat can become rancid very rapidly.

4.1.2.5. Maillard, Strecker, and Caramelization Reactions. We all know from experience that flavor develops when we cook (heat) our food. Thus, the most important reactions, from the perspective of flavor development, are those that are thermally activated. Among these, the Maillard, Strecker, and caramelization reactions are largely responsible not only for the characteristic flavors of cooked meats; but also for the flavors of chocolate and coffee as well the caramel flavors of cooked sugars in sweets and on the crust of freshly baked breads, etc. All of these flavors are produced

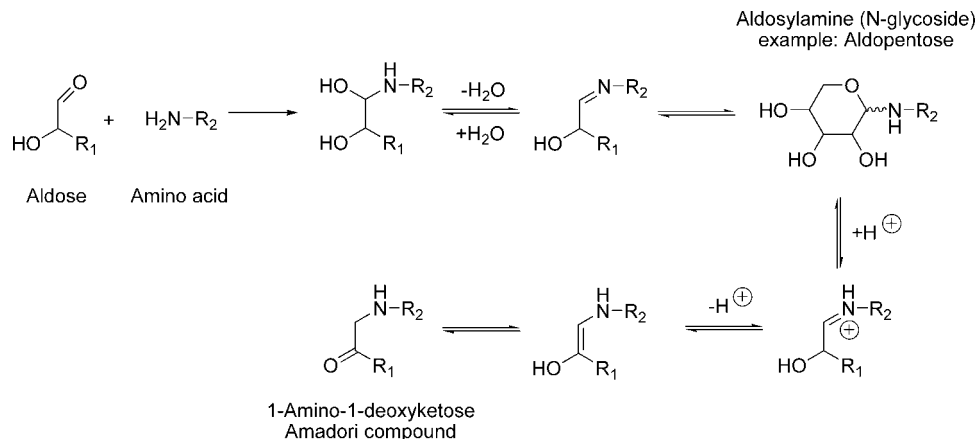


Figure 6. Initial phase of the Maillard reaction showing the formation of Amadori compounds.

in chemical reactions and as such are not natural, although most people would regard these flavors as completely natural while considering some extracted essential flavors (from, for example, citrus fruits) which may be added back into food products as artificial. It will be one of the challenges of Molecular Gastronomy to educate people (domestic cooks, chefs, and the wider public) to understand better how flavors arise and appreciate the very subtle differences between so-called “natural” and “synthetic” products.

When foods are heated, reducing sugars and other carbonyl compounds together with amino acids (or other amines including peptides and proteins) undergo a complex network of reactions that produce both volatile and higher molecular weight compounds including colored pigments and heterogeneous polymers. The formation of brown products on heating aqueous mixtures of amino acids and sugars was first described by Louis Maillard in 1912. Since then, Maillard reactions have been subject to many studies in foods and model systems. Maillard and related reactions are complex and difficult to understand fully or predict. However, we do now have a fairly detailed understanding of the reaction pathways involved as well as the role of the reaction products in flavor, browning, and nutrition. Further, the antioxidative, toxicological, and antimutagenic properties of many of the products of these reactions are now reasonably well documented.¹²⁵

Of course, most foods are complex systems with many components that can react when heated. Accordingly, the Maillard reaction often occurs in parallel with other reactions such as the Strecker reactions and caramelization of sugars. Maillard reactions have also been implicated with thermal degradation of lipids, leading to the lack of the desirable flavor generation by producing heterocyclic compounds with aliphatic side chains.¹²⁶

4.1.2.5.1. Principal Mechanisms of Maillard and Associated Reactions. The Maillard reaction has been divided into three stages, consisting of the condensation of an amine with a reducing sugar, to produce an N-substituted glycosylamine. The subsequent Amadori (for aldoses) or Heyns (for ketoses) rearrangement then produces isomeric compounds. These unstable compounds give neither browning nor aroma but serve as important precursors for subsequent reactions (Figure 6). The second stage involves the enolization of the Amadori and Heyns products and elimination of the amino compound under formation of 1-deoxyosones or 3-deoxyosones. These compounds subsequently undergo dehydration and fragmentation reactions when sufficient heat is provided.

The Amadori product can be broken down by either of two pathways. The 1,2-enolization is promoted by protonization of the N atom in the Amadori compound, which is favored under acidic conditions and leads to formation of a 3-deoxyosone. In a more alkaline environment, protonization of the Amadori compound is less effective and, thereby, indirectly stimulates the 2,3-enolization.^{127,128} Alkaline conditions thus favor the formation of hydroxyfuranones via the 2,3-enolization and formation of a 1-deoxyosone (Figure 7).

In the dehydration of the deoxyosones, furfurals and/or furanones are formed. Furthermore, the fission of deoxyosones, e.g., by retro-aldolization, may produce a range of carbonyl compounds such as acetaldehyde, 2-oxopropanal, hydroxypropanone, and butanedione.¹²⁸ An example of the degradation of the deoxypentosone is given in Figure 8. It is at this stage of the Maillard reaction that many different flavor compounds develop in a network of competing reactions.

The formation of reductones and fission products in the Maillard reaction is associated with the Strecker degradation of amino acids. This reaction involves condensation of α -amino acids with conjugated dicarbonyl compounds to

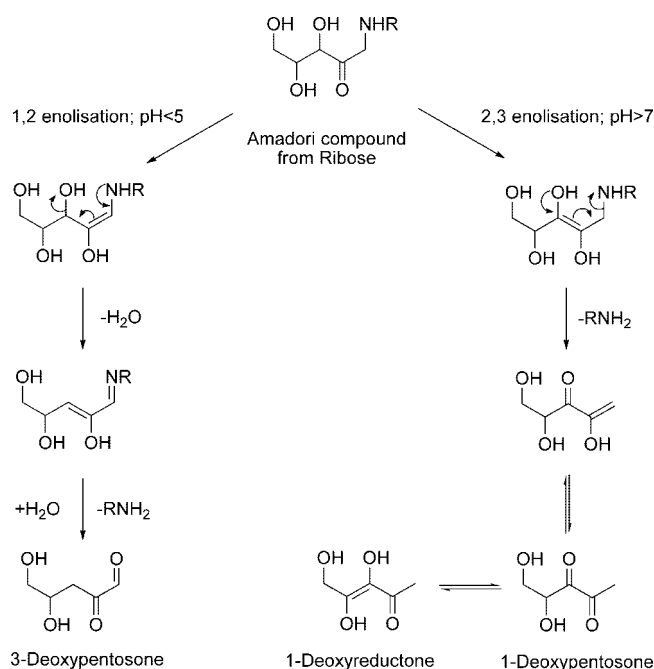


Figure 7. Enolization of the Amadori compounds under different pH conditions.

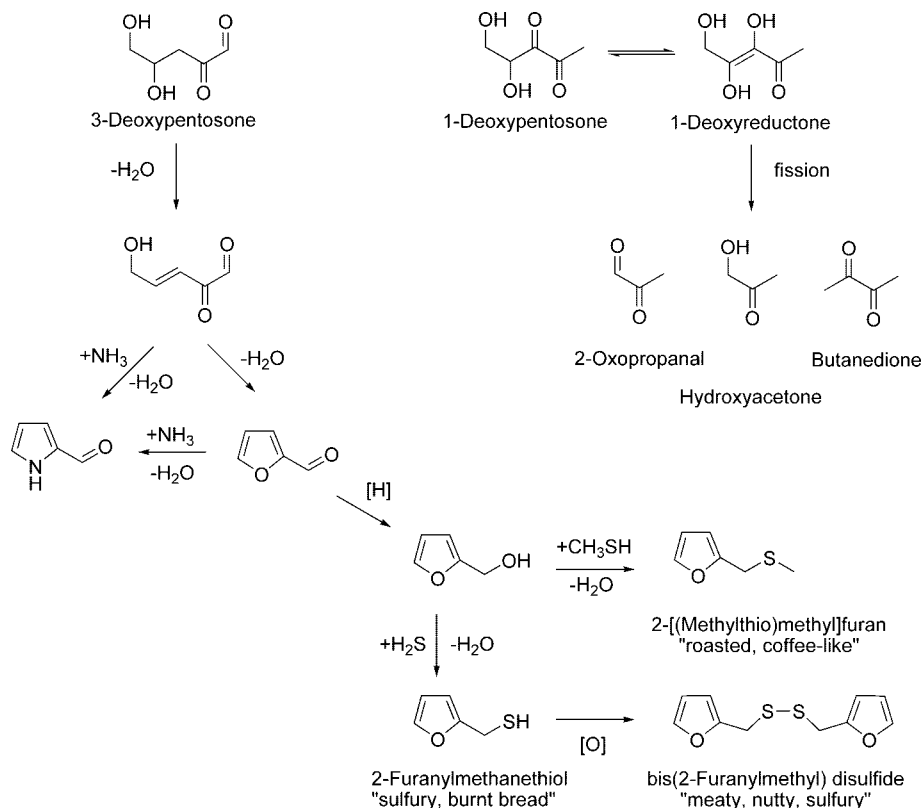


Figure 8. Some possible degradation products from deoxypentoses found in cooked foods. These compounds may also derive from other pathways in the Maillard reaction.

form a Schiff base, which enolizes into amino acid derivatives that are easily decarboxylated. The new Schiff base with one atom less is then split hydrolytically into an amine and an aldehyde which correspond to the original amino acid with one carbon atom less. The net result of the Strecker degradation is a transamination which could be an important reaction for the incorporation of nitrogen into melanoidins.¹²⁹ Secondary amino acids such as proline and hydroxyproline resist Strecker degradation because of the blocked transamination. However, in heating reactions with sugars, proline is an important precursor for compounds with cereal-like flavor notes. The Strecker reaction of cysteine results in the generation of ammonia, ethanal 2-mercaptoethanal, and hydrogen sulfide, which are important precursors for the heterocyclic flavor compounds. Methionine can also undergo further degradation by forming ammonia, methional, methanethiol, and dimethyl disulfide.¹³⁰ The aminoketones formed during Strecker degradation can through condensation reactions form different kinds of alkylpyrazines, which are typically found in toasted/roasted foods such as nuts, bread, and meat.¹³¹

The intermediate stage of the Maillard reaction and related reactions provides a complex pool of reactive compounds, which are subjected to rearrangements and further reactions producing several classes of heterocyclic (volatile) products, several of which are important for cooked flavor. This can be characterized as the final stage of the Maillard reaction, which also comprises the irreversible conversion of carbonyl compounds, e.g., by retro-aldolization with or without involving amines into high molecular weight (brown) heterocyclic (co)polymers, the melanoidins.

Caramelization of sugars also gives rise to browning and generation of volatile flavor compounds and involves enolization, dehydration, and fragmentation pathways. Dehydra-

tion of sugars producing 2-furfural (from pentoses) and 5-hydroxymethyl-2-furfural (from hexoses) occurs at temperatures greater than 150 °C. At higher temperatures colored pigments and a number of volatiles are generated, including furans, carbonyl compounds, etc.¹³² In the Maillard reaction, amines allow such reactions to take place under milder conditions and in addition serve as a source for other heterocyclic compounds to be generated.¹³³

In addition to the classical pathways in the Maillard reaction, alternative routes have been proposed. Some of these reaction schemes involve the early stage of the reaction such as the double substitution of the amino-deoxy-ketose with subsequent regeneration of the amino acid.¹³⁴ Other pathways include an early cleavage of the sugar moiety of the Schiff base prior to Amadori rearrangement. This route seems to occur at neutral and alkaline pH and involves formation of C₂ and C₃ carbonyl-alkylamine fragments that may condense to N-heterocyclic polymers.^{135,136} Mechanistic studies using [¹³C]-labeled sugars have provided more details of possible fragmentation routes of the sugar moiety in the Maillard reaction.^{137–139}

4.1.2.5.2. Interactions with Lipids. Several studies have pointed out the participation of compounds from lipid degradation in the Maillard reaction. A number of volatiles have been identified, with the majority known as long-chain alkyl-substituted heterocycles with nitrogen and/or sulfur in the ring. The mechanisms for the formation of these lipid–Maillard interaction compounds from foods and model systems have been reviewed elsewhere.¹²⁶ The flavor characteristics of some of these alkyl-substituted heterocycles have been described by ‘fatty’, ‘tallow-like’, ‘green’, ‘vegetable-like’ terms,¹⁴⁰ however, their odor threshold values are generally much higher than the Maillard compounds contributing with desirable flavor notes. Thus, when compet-

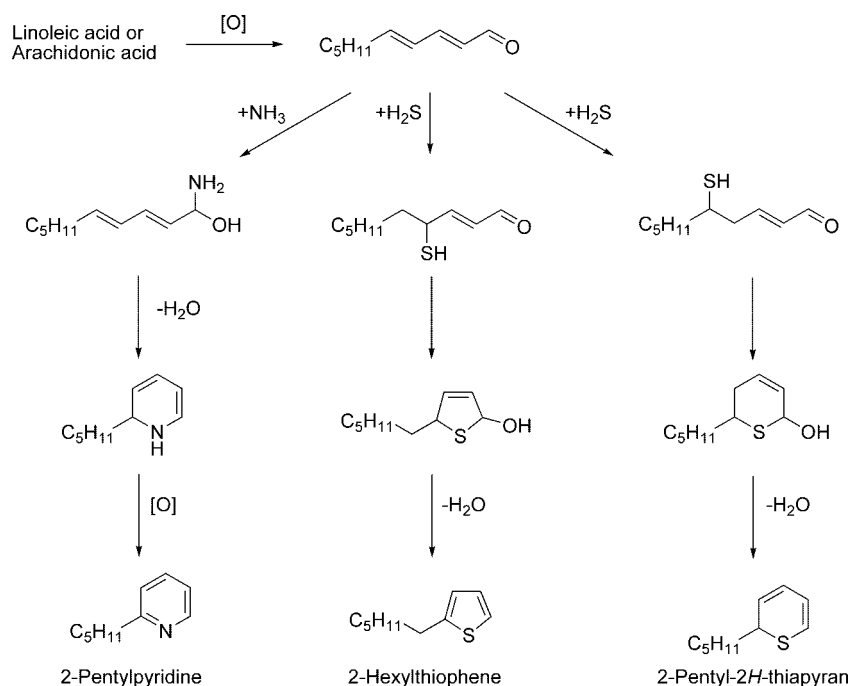


Figure 9. Schematic reaction pathways of 2,4-decadienal from polyunsaturated fatty acids with hydrogen sulfide or ammonia yielding long-chain alkyl-branched heterocyclic compounds (after Farmer and Mottram¹⁴³).

ing for reaction intermediates, lipid degradation products may decrease the Maillard flavors during cooking. The levels of unsaturated fatty acids and conjugated alkenals may be important for these reactions to occur.

An example of the reaction of 2,4-decadienal with ammonia or hydrogen disulfide leading to the formation of 2-pentylpyridine, 2-hexylthiophene, and 2-pentyl-2H-thiapyran is given in Figure 9. In baked cereals *n*-ethyl, *n*-butyl, and *n*-pentyl 2H-thiapyrans have been identified when levels of secondary lipid oxidation products were relatively high.¹⁴¹ In cooked beef from cattle fed diets supplemented with fish oil or linseed oil Elmore et al.¹⁴² found many alkylthiazoles and alkyl-3-thiazolines. The substituents in positions 4 and 5 were methyl or ethyl groups, while the 2-position contained isopropyl, isobutyl, and C4–C9 *n*-alkyl groups. The concentrations of 2-*n*-alkyl-3-thiazolines were much higher in the steaks from the cattle fed with fish oil supplements than in the control samples. These 3-thiazolines may also form from the interaction of intermediates of the Maillard reaction with aldehydes derived from lipid degradation.

4.1.2.5.3. Factors Affecting the Rate and Direction of the Maillard Reaction. The Maillard reaction has been shown to be strongly dependent on the reaction conditions and availability of reactants throughout the food. The most important parameters affecting the generation of aroma volatiles are combinations of temperature–time, moisture content, pH, and type of amine and carbonyl precursors present.^{129,141,144,145} Many foods are heterogeneous materials, and the reaction may be favored or inhibited locally in the product. The reaction often is most severe at the surface of a product, where the water content locally can be reduced and concentrations of precursors increased rapidly. Furthermore, the product surface temperature may locally exceed 100 °C. Water transport from the inner part of the product to the surface during cooking may also contribute to transport of Maillard precursors, such as monosaccharides and amino acids, which decrease due to their reactivity at the product surface. Changes in the physical phases in the food, where

Maillard reactions take place, also contribute to the degree of color and flavor generation in the product. Phase transitions from liquid to rubbery and glassy states significantly affect the course of the reaction. At temperatures below the glass transition temperature (T_g) the rates of browning are generally low and increase at temperatures closer to and above T_g . Different reactivity for monosaccharides has been observed, and the rate of browning is not clearly related to the rate of loss of amino acid.^{146,147} At temperatures below T_g , the limited mobility of small reactant molecules in the glass material may be a limiting factor for the Maillard reaction to occur efficiently.¹⁴⁸

The pH is also an important factor in controlling the Maillard reaction, influencing the reactivity of free amino acids (both thiols and amine groups) and enolization of the Amadori compounds. In cooked meat with relatively small changes in the initial pH (4.0–5.6) rather large changes in the aromas and aroma volatiles have been reported. The total quantity of volatile compounds increased as the pH decreased. A number of furan thiols and their oxidation products were preferentially formed at acid pH; some of these compounds had strong meaty aromas. The formation of other heterocyclic compounds such as thiazoles and pyrazines were favored by higher pH.¹⁴⁹ In extrusion cooking of cereals, changing the pH by addition of sodium hydroxide in the feed also showed significant changes in the range and levels of aroma volatiles; however, these changes were less marked than those achievable by temperature and moisture combinations.¹⁴¹ A summary of changes occurring during the different stages of the Maillard reaction is given in Table 3.

4.1.2.5.4. Maillard-Derived Flavor Compounds and Their Presence in Foods. Flavor formation constitutes quantitatively only a minor pathway in the Maillard reaction, since the majority of the reactants are converted to carbon dioxide, melanoidins, and numerous intermediates rather than volatiles. However, a great number of volatile and nonvolatile compounds may be generated in the Maillard reaction, and many of them have been identified and characterized

Table 3. Changes Occurring during Different Stages of the Maillard Reaction (adapted from Nursten¹²⁵)

changes	initial phase	intermediate stage	final stage
production of color or discoloration	–	+	+++
production of flavor or off-flavor	–	+	++
production of water	+	+	+
lowering of pH	+	+	+
antioxidative activity	+	+	+
loss of vitamin C activity	+	–	–
loss of biological value of proteins	+	+	+
production of fluorescence	–	+	+

sensorial. The aroma volatiles from the Maillard reaction may be classified into three groups to provide a convenient way of viewing the origin of the complex mixture of compounds. The classes of compounds in these groups are organized according to their stage of formation and origin and include (1) simple sugar dehydration and fragmentation products such as furans, cyclopentenes, and carbonyl compounds, (2) amino acid degradation products such as Strecker aldehydes, and (3) products from further interactions.¹³³

A number of these compounds have relatively high flavor threshold values and need to be generated in excess in order to contribute to flavor. However, the compounds belonging to the third group include a wide variety of small, often branched, heterocyclic flavor compounds including pyrroles, pyridines, pyrazines, imidazoles, oxazoles, thiophenes, thiazoles, thiazines, furanathiols, and sulfides. Several of these compounds have rather low odor threshold values, and their aromas are often characterized by ‘nutty’, ‘roasted’, ‘toasted’, ‘cooked vegetable’, ‘caramel’, and ‘meaty’ flavor notes typically present in heat-treated foods as in coffee, chocolate, roasted seeds and nuts, vegetables, meat, and cooked cereals.^{140,150} The mixture of flavor compounds created in the Maillard reaction is usually complex. The contribution of individual compounds to the flavors of the Maillard reaction is difficult to predict, since they can give different kinds of perceptual effects in mixtures, such as suppression, addition, and in few cases even synergy. Furthermore, the compounds can both contribute to odor impressions as well as taste sensations.

In a few instances Maillard compounds have been attributed as major contributors to the typical flavor of foods.¹⁵¹ For example, 2-furanylmethanethiol is an impact compound in the aroma of freshly roasted coffee,¹⁵⁰ whereas 2-acetyl-1-pyrroline and to a lesser degree 6-acetyl-2,3,4,5-tetrahydropyridine have been identified as key aroma compounds in bread crust¹⁵² and popcorn.¹⁵³ The chemistry and occurrence of these and other related potent ‘roasty’ smelling compounds have been reviewed elsewhere.¹⁵⁴ Alkylpyrazines are often an indication of the degree of Maillard flavor development during cooking, although very few of them are generated in sufficiently high amounts to give a contribution to the flavor.

In meat flavor it has been difficult to identify key impact compounds, since meat can be cooked in different ways and originates from different species. Maillard flavors in beef, chicken, and pork flavor have been investigated to a greater extent relative to other species. The Maillard flavors have been shown to depend on the raw meat quality and cooking method, and many different heterocyclic compounds have been identified.¹⁵⁵ The flavor precursors in meat are different

from those in plant materials. This is partly due to the fat content and fat distribution throughout the meat, which can interact with Maillard reactions, but also due to enzymatic reactions post mortem, which often increase the levels of important Maillard precursors. Enzymatic hydrolysis of ribonucleotides including adenosyl monophosphate (AMP) post mortem can lead to relatively high levels of ribose. This aldopentose is an effective Maillard precursor for typical ‘meaty’ flavor compounds with very low flavor thresholds such as 2-methyl-3-furanthiol (MFT) and bis(2-methyl-3-furanyl) disulfide (MFT-MFT)¹⁵⁶ (see Figure 10). Although these compounds have long been known from model reactions of ribose and cysteine, they have also been identified in cooked beef.¹⁵⁷ Further, phosphorylated monosaccharides and peptides are hydrolyzed post slaughter and can yield significantly higher levels during post mortem conditioning of beef.^{157,158} In pork it has been shown that ribose is rather unstable and glucose and fructose are the most likely important Maillard precursors.¹⁵⁹

Studies on the key aroma compounds in beef have shown the importance of the Maillard reaction. In boiled beef, MFT, 2-furanylmethanethiol, 2-acetyl-1-pyrroline, MFT-MFT, and methional were ranked with a relatively high sensory impact together with some lipid degradation products.¹⁵⁷ In roasted beef other Maillard compounds were indicated as sensorially more important and included 2-acetyl-2-thiazoline, 4-hydroxy-2,5-dimethyl-3(2*H*)-furanone, 2-ethyl-3,5-dimethylpyrazine, 2,3-diethyl-5-methylpyrazine, and methional.¹⁶⁰

Although many volatile compounds have been identified in Maillard reaction systems and implicated in the aromas of many foods, their impact to bitter tastes should also be mentioned. Sugar dehydration products such as 2-furfural, 5-hydroxymethyl-2-furfural, and 2-methyl-3-hydroxy-4*H*-pyran-4-one are known to possess bitter tastes as well as a number of alkylpyrazines¹⁶¹ and some thiazoles and thiazolidines.¹⁶²

Products derived from the reaction of carbonyl compounds with proline provide the specific bitter compounds cyclo-[*b*]azepin-8(1*H*)-ones and pyrrolidinyl-2-cyclopenten-1-ones as identified in model proline reaction systems and beer.¹³⁹ Cyclo[*b*]azepin-8(1*H*)-ones and a number of 2,3-dihydro-1*H*-pyrrolidines have also been found in bread crust from dough enriched with proline.¹⁶³ In addition to the volatile compounds from the Maillard reaction, which as well as their aroma also possess a bitter taste, a number of nonvolatile bitter compounds have been identified, e.g., diketopiperazines in cocoa.¹⁶⁴ More recently, bitter-tasting compounds have been identified by taste-dilution analysis, and potent bitter compounds from the Maillard reaction with xylose, rhamnose, and L-alanine have been characterized including 1-oxo-2,3-dihydro-1*H*-indolizinium-6-olates.¹⁶⁵ In particular, the thiophene derivatives show extraordinarily low bitter taste thresholds down to 6.3×10^{-5} mmol/L water.

The Maillard and caramelization reactions provide an excellent means of generating a variety of desirable flavors during cooking of foods. Although many Maillard precursors and conditions have been identified to influence the course of the reaction in different foods, the applications in gastronomy will still depend on experimenting with these to control the desirable outcomes. Although the positive formation of flavors in the Maillard reaction has received much attention, control of the generation of toxic compounds, e.g., imidazoquinolines and acrylamide, also deserve consideration. For example, tryptophan is effective in preventing

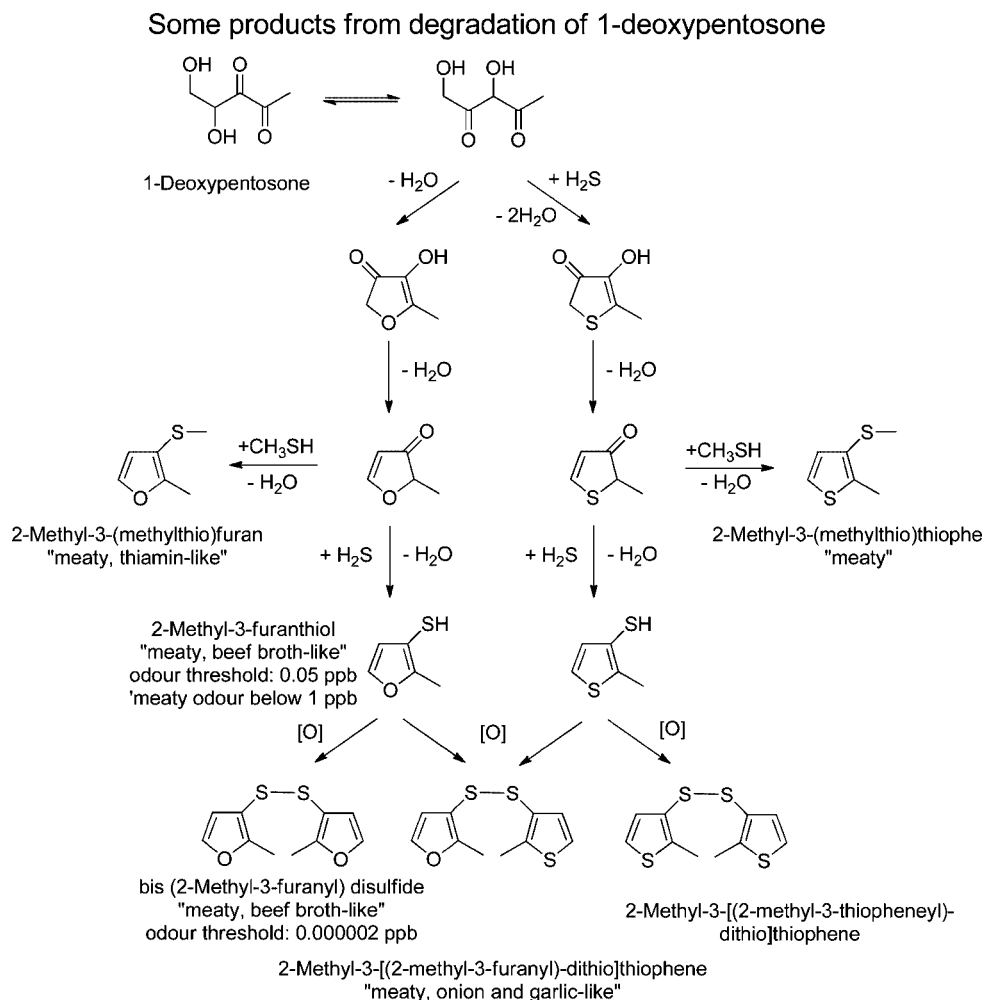


Figure 10. Formation of some important meat flavor compounds from the Amadori product of ribose (modified after Mottram and Whitfield¹⁵⁶).

the formation of imidazoquinolines, and cooking methods can be optimized with regard to acrylamide formation from asparagine. The toxicological aspects of the reaction should deserve attention among gastronomers both from a consumer standpoint and from a chef's standpoint during the preparation of the food. Some toxic compounds may not enter the food, since they are evaporated during the cooking process, but need to be removed efficiently from the cooking environment in protection of the chef's health.

4.1.3. Illustrative Example: Preparing Meat Stocks

It is clear from the foregoing sections that the chemistry of cooking is extremely complex, making it very difficult to predict with any certainty how flavor will develop in any real cooking process. Not only will the ingredients themselves vary from batch to batch but also the actual processing of these ingredients will never be fully consistent in a real kitchen nor will the temperatures and times of the cooking processes. Thus, while we may understand some of the general principles it is unlikely we will ever be able to master cooking simply from the underlying chemistry; this is one reason why chefs always continually taste samples from their dishes as they prepare them. However, it is a worthwhile exercise to examine at least one apparently standard cooking process to see how many of the above reactions occur and attempt to understand how knowledge of the chemical changes occurring during cooking can be translated into the

kitchen environment. To this end, we have chosen the cooking of a basic meat stock as an example.

One of the most remarkable processes in the kitchen is the preparation of a stock; initially flavor molecules are simply extracted from the basic ingredients (meat, vegetables, etc.) in water (or sometimes in wine), but something quite remarkable happens as the liquid is kept simmering: the flavor changes and apparently new flavors develop. More astonishing is the fact that as the simmering continues, the stock is reduced (by evaporation of water), and the kitchen is filled with the aromas of the cooking stock, even more flavor develops. One would naturally expect that the flavor molecules, being volatile, would evaporate, leading to a reduction in the overall flavor of the stock. However, in practice, the process of reducing a stock by slow evaporation actually concentrates and enhances the flavor.

Such a complex process is clearly too difficult to interpret fully, but it serves to illustrate several aspects of the development of flavors discussed above and, in particular, demonstrates the complexity of the nature of the chemistry of cooking. In the various studies we discuss below different recipes were used; some authors use the ingredients of a typical stock, meat, bones, and vegetables all cooked together, while others prefer to try to isolate the importance of particular ingredients and so tend to prepare a stock using only the meat (or the meat and bones) without the vegetables.

When studying a recipe for a stock a lot of things can be questioned: does it matter when the salt is added? Is the initial temperature of the water important? What is the effect of the time of cooking? How does the ratio of the meat to the bones affect the final product? And so on. When the stock is further boiled down (reduced) to make a concentrated liquid, further issues arise including which flavor compounds are lost through evaporation and which are formed in the pot during cooking.

Recipes will often tell you to start with cold water and bring the pot to simmer, regularly skimming off fat and scum. According to McGee,¹⁶⁶ starting with cold water allows soluble proteins to escape the solids and coagulate slowly, forming large aggregates that either rise to the surface and are easily skimmed off or settle to the bottom and sides. A hot start produces many separate and tiny protein particles that remain suspended and cloud the stock, and a boil turns particles and fat droplets into a cloudy suspension and emulsion. The reason for recommending to leave the pot uncovered is according to McGee:¹⁶⁶ it allows water to evaporate and cool the surface, which makes it less likely that the stock will boil. It also dehydrates the surface scum, which becomes more insoluble and easier to skim. Further, it starts the process of concentration that will give the stock a more intense flavor.

A lot of research has been concerned with the flavor of beef and attempted to identify the key aroma components constituting the beef stock aroma.^{167–169} There has been considerable similar research on other types of meat such as chicken and seafood.^{170,171} To identify the important aroma and taste compounds in a given food it is necessary to have appropriate techniques for separating the volatile and non-volatile compounds (chromatography) and identifying the components as well as method for determining the sensory impact of these (GC-Olfactometry, a method where a panel of trained subjects evaluate the quality and intensity of GC effluents). Less research has been carried out on the cooking process of the stock, although some studies have been concerned with the cooking procedures of the stock and the difference it makes for the flavor of the stock.

On the basis of cookery books, Seuss et al.¹⁷² hypothesized that the temperature progress during stock cooking is important for the resulting flavor. They investigated the effect of temperature and cut size (minced meat vs small cubes) on the flavor of beef stock as well as on several nonvolatile compounds. They found that the best flavor, as determined by a sensory panel, was obtained when cooking at 85 °C. The authors recommend cooking the broth at a temperature below the boiling point since they find that the stock cooked at 95 °C becomes less strong in meat flavor and more bitter. In general, positive sensory assessments were related to a high concentration of inosine monophosphate, inosine, lactate, and free amino acids. The difference between minced meat and small cubes of meat (2 cm) was found not to be important for the flavor.

Cambero et al.¹⁷³ also studied the flavor of beef stocks as affected by cooking temperature and identified some of the compounds responsible for the brothy flavor. In correspondence with Seuss et al., they found that the brothy flavor was strongest when cooking at 85 °C (based on four trained judges). The chemical analyses showed that a wide mixture of free fatty acids, peptides of low molecular weight (<300 Da), and IMP all had an important role in the flavor intensity of the beef broth.

The relationship between beef stock components and the flavor developed at different cooking temperatures has been further studied by Cambero et al.¹⁷⁴ The combined sensory study (descriptive analysis and rank order test with 9 trained panelists) with chemical analyses showed a significant increase of small non-amino acid nitrogen compounds, creatine, GMP, IMP, and AMP with beef stock flavor intensity. The beef stock obtained at 85 °C was found by sensory analysis to have the most acceptable flavor, presumably related to the free sugars and amino acids and their reaction products. Stocks produced at temperatures higher than 95 °C displayed off flavors which were easily detected by the sensory panel.

Furthermore, Cambero et al.¹⁷⁵ investigated the flavor development of beef stock in more detail by studying the effect of the cooking temperature, cooking time, ratio of meat and water, and NaCl concentration. They found that the cooking temperature is important since less intense heat treatments generated raw meat, bloody, and metallic flavors whereas stocks prepared at higher temperatures generated sour, astringent, and warmed-over flavors (WOF). Stock obtained at higher temperatures needed a shorter cooking time to obtain a good flavor; however, it was concluded that temperature plays a more important role than cooking time in the generation of the sensory properties of a good beef stock. The best stock was obtained by cooking at 85 °C for 60 min with 7.5 g/L salt with a ratio of 1:2 (meat:water by weight).

Pereira-Lima et al.¹⁷⁶ performed a similar study on the flavor of beef stock, comparing the sensory results with chemical data (amino acids, free fatty acids, and the dipeptides carnosine and anserine) on stocks cooked at various conditions (cooking temperature and time). A positive relationship is seen between a good beef stock flavor and increased levels of Glu, Asn, Lys, and Met. An inverse relationship to beef stock flavor was found with Cys, Pro, Ser, M-His, Tyr, Val, Arg, and Asp, which could be interpreted as a positive relation of the reaction products (Maillard, Stecker) of these and stock flavor. The amounts of the dipeptides, carnosine and anserine, increase significantly with increasing cooking temperature but not with the cooking time. Sensory evaluation shows that increased carnosine and anserine levels provide an improved flavor.

In a later study by Cambero et al.¹⁷⁷ they investigated the effect of cooking conditions on the flavor of shrimp stocks. They studied various NaCl concentrations, shrimp–solutions ratios, cooking temperatures, cooking time, and shrimp preparations in order to determine the cooking conditions that yield the best stock flavor. Best stock was obtained by using whole shrimp in 0.5% NaCl solution (1:2) at 85 °C for 30 min. The stocks were evaluated by a sensory panel (11 trained panelists, rank order test), and the chemical composition was analyzed. Boiling was found to cause the formation of off flavors. The free fatty acids were found to be very important for sensory evaluation of the stocks (the best stocks had the highest level of FFA). Overall temperature was found to be more important than time, just as with the beef stock study by the same author.

In the kitchen the preparation of stocks is one of the most important operations; stocks form the basis of nearly all sauces, so that chefs devote a great deal of time and effort to their preparation. Cookery texts differ greatly on the best methods to use when preparing meat stocks; for example, some indicate it is essential to put the meat in cold water

and heat up, while others permit meat to be put directly in hot water; some suggest meat should be browned before boiling whereas others do not. Most cookery tests suggest “simmering” rather than boiling, which indicates they may be suggesting using a low temperature to achieve a better result. As yet, it is very difficult to draw any definite conclusions about the relative merits of such diverse methods of stock preparation. However, a few general principles do emerge from the limited scientific studies to date. For example, the fact that the amount of dipeptides created depends more on the temperature than the time immediately suggests there may be benefits from cooking stocks in a pressure cooker where temperatures well in excess of 100 °C can be used; indeed, this is the technique used for most stock production at several restaurants¹⁷⁸ or for longer times at much lower temperatures (no higher than 90 °C), which is not a technique used in any kitchen that we are aware of.

4.2. Color of Food

As we shall see later, our perception of the flavor of food is influenced by many factors other than detection of the actual aroma and taste molecules released by the food itself. One of these is the color of the food. Color sets up an expectation of the flavor: red fruits seem to be riper, green vegetables fresher, and (for some) purple meats more perfectly cooked. Thus, it is worth reviewing some of what we know about how the color of meats, fruits, and vegetables changes during processing so that we may, to some extent, control the changes to provide the diner with a dish that has the most acceptable color. We begin with the better studied area of the color of meat and then move onto look at fruits and vegetables.

4.2.1. Color of Meats

In modern retail, the quality of meat is often judged by its immediate appearance; thus, any apparent discoloration of meat is, for many consumers, the primary reason for rejection of a specific product. During cooking color changes are further used to follow the progression of heat treatment, and when served, meat is expected to have a characteristic color appearance depending on the actual meat product, heat treatment, dish of which the meat is a part, and personal preference of the diner. For example, the internal color of a steak is used by many as an indicator of its “doneness”, a purple color indicating a rare steak, red a medium steak, pink well done, and gray or brown showing the steak is overcooked.

The color of meat is dominated mainly by myoglobin, the heme protein with the physiological function of oxygen storage in muscles. The attractive cherry red color of meat is due to a steady-state concentration of oxymyoglobin, which in a specific acid-catalyzed process is oxidized to the brown metmyoglobin, a process which is often termed autoxidation.¹⁷⁹ The steady-state concentration of oxymyoglobin is maintained as long as the metmyoglobin reductase enzyme complex can use the reducing cofactor NADH for reforming the iron(II) form of myoglobin in a process which notably is less dependent on acidity than the autoxidation.

Myoglobin, which is violet, is further converted back to oxymyoglobin, when oxygen is available. The steady-state concentration of oxymyoglobin is thus dependent on pH, as decreasing meat pH accelerates autoxidation more than it accelerates enzymatic reduction of metmyoglobin. The steady-state concentration of oxymyoglobin is also dependent

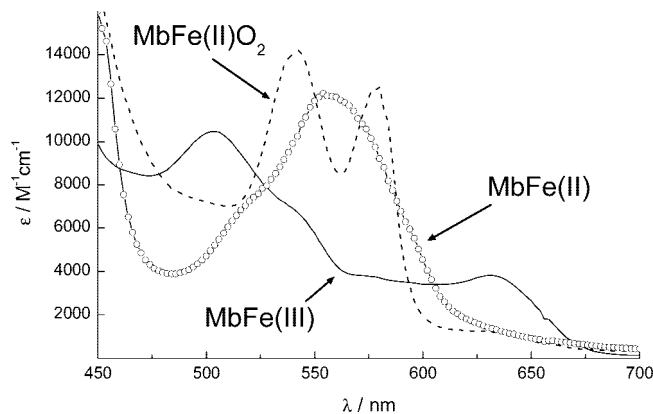


Figure 11. Absorption spectrum of the various forms of myoglobin.

on the presence of reducing cofactors together with enzyme activity, as depletion of reducing cofactors or inactivation of enzymes will block the reduction back to the iron(II) state.¹⁸⁰ An example of the absorption spectra of some different forms of myoglobin is presented in Figure 11.

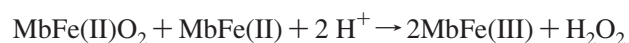
Further, salting decreases the steady-state concentration of oxymyoglobin, as the acid-catalyzed autoxidation shows a positive kinetic salt effect in agreement with protonization of the positively charged iron center as rate determining.^{179,180} The balance between the violet and red form of iron(II) myoglobin depends on oxygen pressure. At the meat surface, the red oxymyoglobin dominates, while in the interior of the meat, where metabolic activity depletes oxygen, the violet myoglobin determines the color.

The strong oxidant oxygen is coordinated to the reducing iron(II) center of the porphyrin, which invariably carries the risk of one-electron transfer, creating the superoxide radical anion and metmyoglobin, the brown and physiologically inactive iron(III) form of myoglobin.^{180–182}

Most people associate a brown color in uncooked meat with spoilage and will reject it. However, a brown color in cooked meat is associated with doneness; the browner the meat the “better” it is done and the “safer” it is to keep. Thus, we tend to rely on smell to detect spoiled cooked meat on storage.

In the kitchen, the spectacular color changes are easily observed by cutting a piece of beef. Once the violet interior is exposed to the air it soon turns cherry red, and a similar bloom on the meat surface may be seen when a pack of vacuum packed beef is opened, allowing oxygen to reach the surface.

A careful inspection of freshly cut beef shows that the three myoglobin forms can be located within the meat by their colors: in the interior the violet myoglobin is separated from the cherry red oxymyoglobin on the surface by a narrow brown ribbon of metmyoglobin. Formation of metmyoglobin has a maximal rate in meat where the partial oxygen pressure makes oxymyoglobin and myoglobin concentrations equal due to the dominating bimolecular electron transfer to oxygen to yield hydrogen peroxide:¹⁸³



It is the balance between oxygen diffusion into the meat matrix from the surface (which generally follows Ficks law) and the rate of oxygen consumption by residual metabolic activity in the meat that determines the depth at which the two iron(II) forms of myoglobin have equal concentration

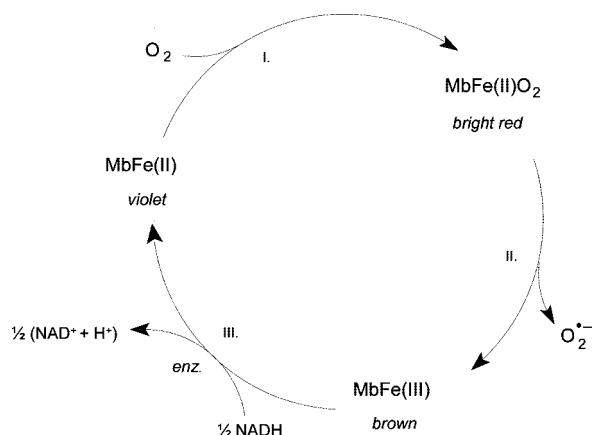


Figure 12. Color cycle of meat.

and at which the rate for metmyoglobin formation is highest.¹⁸³

Meats are probably the most perfect and complete protein source for human nutrition and provide endless possibilities of creation of meals with superior eating experience; thus, the production of meats of the highest possible quality in an ethical and widely acceptable fashion is a matter with which we should all be concerned. In this context, it is notable that an animal which is unstressed at the abattoir prior to slaughter has a high level of muscle glycogen, which in turn provides high levels of reducing cofactors in the meat with a high glycogen content, known to have better color quality.

Thus, we can, in principle, use the color of meat before and during cooking and later during eating the meal as an indicator of the ethical and acceptable production of the meat. Free-ranging animals such as pigs in the Iberian oak grooves or grazing cattle in highland regions eat a forage with a high tocopherol content, which further protects pigments and lipids against oxidation in the meat during storage and cooking, again providing a direct link between the way animals are raised and the quality of the meat we experience during cooking and in the meal.

The production of hydrogen peroxide in meat as the result of the dynamics of the meat color cycle or from lactic acid bacteria present on meat surfaces further affects the proteins and lipids. Hydrogen peroxide can oxidize metmyoglobin to hypervalent iron forms of myoglobin, which are highly pro-oxidant. Perferrylmyoglobin, a formal iron(V) compound, can thus initiate lipid oxidation, while ferrylmyoglobin, an iron(IV) compound, can cleave preformed lipid hydroperoxides.¹⁸³ The peroxidation cycle of myoglobin, which is linked to color cycle as may be seen in Figure 12, accordingly provides a coupling between pigment oxidation and lipid and protein oxidation in meat.^{184,185} Persisting brown discoloration of meat thus indicates that the reducing cofactors in the product are becoming depleted and that accumulating metmyoglobin is now available for conversion to hypervalent and prooxidative myoglobins. NADH and other reductants are also efficient scavengers of the hypervalent myoglobin in effect protecting the lipids and proteins against oxidation. Meats with such persistent brown discoloration are likely to be tough to eat and have unpleasant flavors. The depletion of reducing cofactors is a direct indication of initiation of lipid oxidation, leading to meat rancidity, and of oxidative protein dimerization, leading to decreased tenderness.

In Norway it was legal and a common practice until very recently to pack meat in an atmosphere with a low level of carbon monoxide, which binds very strongly to iron(II)

myoglobin.¹⁸¹ Carbonylmyoglobin is intensely red and does not oxidize to metmyoglobin under normal conditions, so the meat products have a remarkable color stability, which was appreciated in the country with its many remote and small societies and difficult transportation of foods.

This practice is now being introduced for master packs of retail meats in the United States in order to achieve better color stability of fresh meat. The formation of carbonylmyoglobin, however, blocks the color cycle of meat, and the color is no longer a direct indicator of the oxidative status of the product. Moreover, the color changes associated with cooking become different, and color as a doneness indicator becomes corrupted.¹⁸⁶

In other countries, some meat products are now being packed for the retail trade in a controlled atmosphere with a high oxygen content of up to 80% in order to increase the depth of the oxymyoglobin layer of the meat and accordingly to improve the red appearance of the meat.¹⁸⁷ Such practice has, however, been shown to increase lipid oxidation in meat and also oxidative dimerization of myosin, a meat protein of importance for meat tenderness.¹⁸⁷ For a specific meat product the benefits of using a controlled packaging atmosphere should accordingly always be compared to any other effects introduced in relation to product quality.¹⁸⁸

Over the years the curing of meats has developed from simple salting to preserve meat into a major industry. Along the way, the introduction of degraded organic material containing nitrate into the salt serendipitously led to the modern use of nitrite and nitrate in brine curing. This curing method not only preserves the meat but also creates an appetizing red color. The importance of the color aspect of the curing is recognized in the German term “umrotung” for the process. The pink color of cured meat is due to nitrosylmyoglobin, an iron(II) form of myoglobin with nitric oxide coordinated, formed by reduction of nitrite by added ascorbate or inherent reductants like NADH present in the meat.¹⁸⁹ Nitrosylmyoglobin is an antioxidant,¹⁹⁰ in contrast to oxymyoglobin, which is a prooxidant. Discoloration of cured meat as seen upon light exposure in the presence of oxygen should accordingly be avoided, and a brown or gray discoloration of cured meats indicates that the oxidative protection by nitrosylmyoglobin has gone. As long as the meat has a reductive capacity, nitrosylmyoglobin may, however, be reformed and the cured meat still has resistance against lipid and protein oxidation. The antioxidative cycle of nitrosylmyoglobin as associated to the product color is seen in Figure 10.

Parma ham, by contrast, is produced without nitrite or nitrate, and oxymyoglobin is converted by an unknown reaction sequence to zinc–protoporphyrin, which is the principal colorant of this type of dry cured meat.^{191,192} For dry cured hams made with the use of nitrite the pigment transformation to the zinc pigment is completely blocked by an unknown mechanism. In Parma ham from Italy and in the similar Serrano ham from Spain the iron liberated from myoglobin by zinc apparently becomes immobilized or otherwise inactivated, since these dry-cured meat products are surprisingly resistant to lipid oxidation, which is normally catalyzed by simpler iron compounds including Fe(II) and Fe(III) ions. The high gastronomic value of these dry cured hams depends on very complex chemical transformations in the meat matrix during the long maturation period of up to 18 months, which are only poorly understood but should be explored for use in other processed meats.

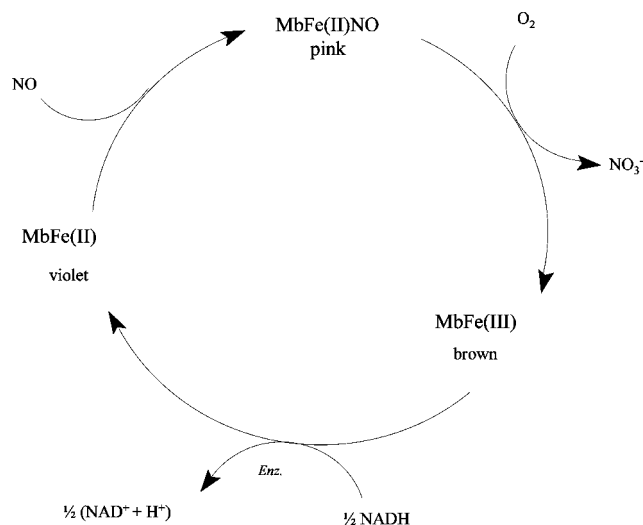


Figure 13. Nitrosyl myoglobin is rather sensitive to the combination of oxygen and light but may be reformed as long as there is a residual reducing capacity remaining in the meat.

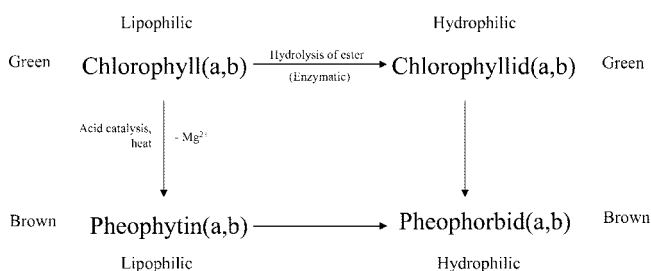


Figure 14. Diagram illustrating how the color of chlorophyll is affected through various degradation mechanisms.

4.2.2. Color of Fruit and Vegetables

The pigments of fruit and vegetables play important physiological roles in the living plants. The chlorophylls match the spectrum of sunlight for optimal conversion of light energy to chemical energy in the plant. At the same time, we have adapted so that the green color provides an indication of freshness while a fading green color acts as a sign of withering. The blue, red, and yellow pigments in plants belong to several classes of chemical compounds of which the carotenoids and polyphenols are the most important.¹⁹³ Carotenoids are associated with the chlorophylls as auxiliary light-harvesting pigments in photosynthesis and are quenchers of singlet-oxygen and scavengers of free radicals for protection during high flux of light.^{194,195} Polyphenols have functions as filters for UV light and as protectors against insect attack, form a part of the enzymatic wound protection system, and are antioxidants.¹⁹⁶

As we have already noted, man's appreciation of vegetables is strongly influenced by the green color. Chlorophyll, in either the so-called a or b form, may degrade by either of two types of reactions during storage and cooking. In an acid-catalyzed reaction, chlorophyll will lose the magnesium ion coordinated in the porphyrin, resulting in a color change from bright green to dull brown¹⁹⁷ (Figure 14). In the kitchen this color change may be prevented by using slightly alkaline water for boiling of green vegetables, which may be obtained, for example, by the addition of baking soda. Chlorophyll is lipophilic and anchored in the lamellae of the chloroplasts. Enzymatic hydrolysis of the phytol ester converts chlorophyll to the hydrophilic chlorophyllide in a process which occurs

post harvest and increases leaching of green color from leafy vegetables during cooking.

The lipophilic character of chlorophyll is recognized in the much appreciated green color of virgin olive oil. However, the separation of chlorophyll from the carotenoids of the chloroplast makes the oil sensitive to light exposure, since the chlorophyll acts as a photosensitizer generating singlet oxygen, which then oxidizes oleic acid, resulting in a hay-like off flavor. The (physiological) function of chlorophyll in vegetable oil becomes uncoupled from the function of carotenoids as protectors against radicals and singlet oxygen, a protection which is highly important in the fruits of the olive tree during sun exposure.

Carotenoids are only synthesized in plants and algae and in the kitchen provide the appetizing red color of ripe tomatoes and carrots. However, carotenoids are transferred along the food chain, providing color to other organisms.¹⁹⁵ For example, in the oceans, astaxanthin synthesized by phytoplankton is transferred to krill and eventually to shrimp and salmonids, providing them all with their distinctive reddish pink coloration. In Japanese kitchens the red color of shrimp is highly admired and any white spots of ikaite, a calcium carbonate hydrate formed during frozen storage in the shell, is considered as a serious defect although it is without effect on flavor.¹⁹⁸

In most cultures, a pink salmon color is likewise appreciated in dishes prepared from smoked or boiled salmon or trout. Trout and salmon are increasingly being farmed in order to meet demands of the world markets. In such farms the pink pigmentation is ensured by the addition of carotenoids to the fish feed. The physiological function of astaxanthin in the flesh is uncertain, but a uniform pigmentation is considered to indicate high quality.

Carotenoids are, however, distributed unevenly in various tissues in most organisms that absorb them. Indeed, the pigmentation of many foods is affected greatly by seasonal (and other) variations in the availability of carotenoids in the diet. Structures of some of these compounds are illustrated in Figure 15. A good example, which is likely to be noted by chefs as well as domestic cooks, is the variability of the color of the yolks of hens' eggs. Depending on the diet of the hen the yolks may vary in color from pale yellow to bright red; generally, free-range hens that have access to a range of feeds tend to eat more colorful foods and produce darker and redder egg yolks.¹⁹⁵

Flavonoids and anthocyanines are examples of polyphenols important for the color of flowers and fruits. Apples which have been damaged by insects will turn red faster, indicating the protective role of the polyphenols in the living plants. In the kitchen the yellow, red, and violet colors of berries are important for deserts of various types and fruit drinks. Normally, fresh fruits have acceptable color stability, but upon preservation colors made fade. During canning, tin from metal cans will sometimes dissolve and form complexes with anthocyanines from the fruits, in effect stabilizing the color.¹⁹³ Anthocyanines have color, which varies with pH, so that red colors will dominate under acidic conditions as in desserts or fruit smoothies with addition of lemon juice. Such color variations allow the chef the opportunity to change the color of such fruits simply by changing the level of acidity. For anthocyanins the effect of pH on color is due to the complex acid/base equilibria depicted in Figure 16. The acid form of the anthocyanin is in mutual equilibrium with the corresponding base and with a pseudobase, the latter

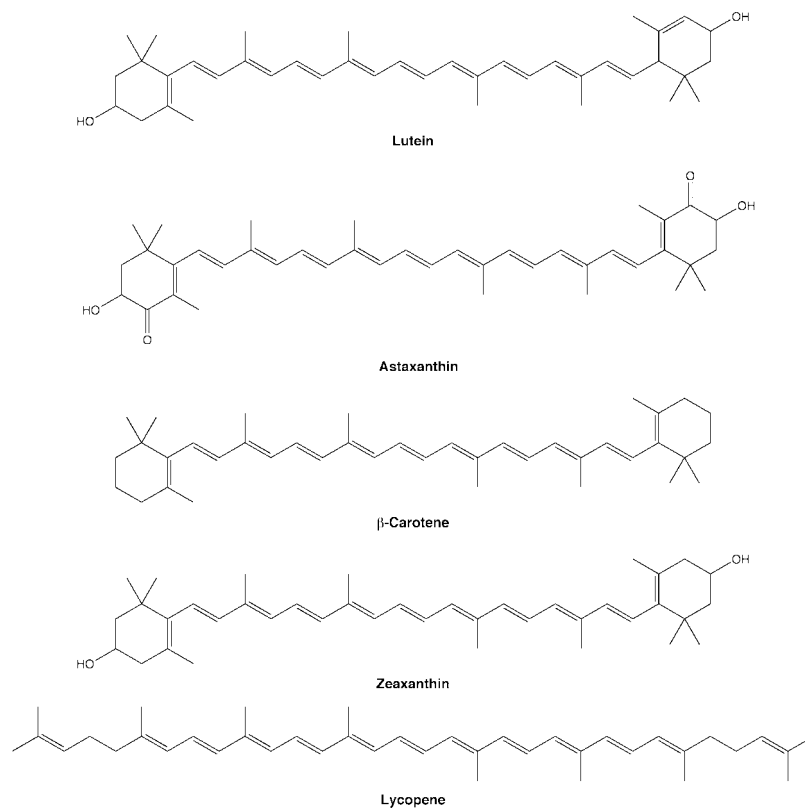


Figure 15. Lycopene from tomatoes and carotene from carrots is red, while lutein and zeaxanthin, classified as xanthophylls (oxygen containing), are yellow. Astaxanthin is the pink colorant in salmon.

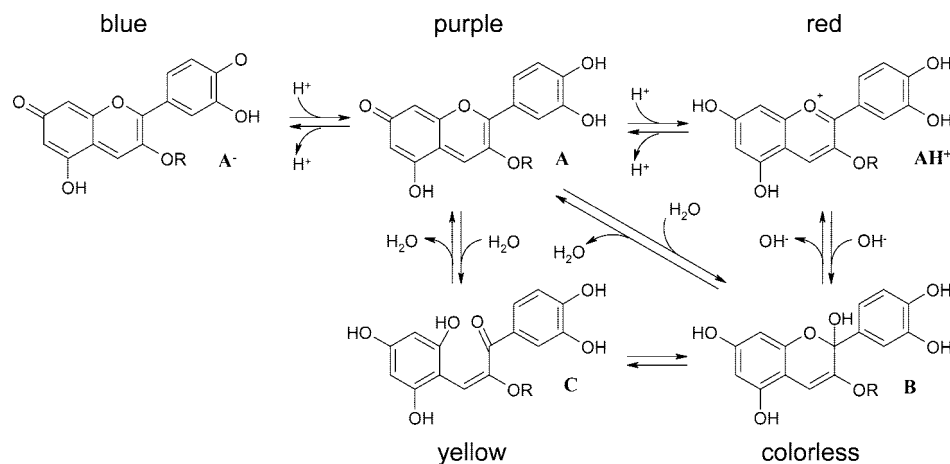


Figure 16. Equilibria between different forms of anthocyanins affecting color. AH⁺ is a flavylum cation, A is the quinoidal base, A⁻ is the ‘anhydro’ base, B is the pseudobase, while C is the chalcone.

formed by addition of a hydroxyl ion. The equilibrium between the pseudobase and the base is independent of pH but depends on water activity. The heterocycle of the skeleton may open for both the base and the pseudobase. The equilibria are further complicated by molecular stacking phenomena, which further affects color. In the kitchen pH is easily controlled, and colors of fruit-based desserts or drinks may accordingly be adjusted.¹⁹⁹

4.3. Textures in Food and How To Make Them

The overall appeal of any food is determined not only by its flavor but also, to a large extent, by its texture. For example, some foods need to be crisp and crunchy to be properly enjoyed. No matter how good the flavor a “soggy” potato chip (crisp in the United Kingdom) will not taste right;

ice creams that are not properly smooth due to large ice crystals have an unappealing gritty texture, while a limp salad will put off even the least discriminating diner. The control and modification of texture is therefore an important aspect of the kitchen repertoire and well worth discussing in some depth.

Chefs know how to modify the texture of meats to produce crisp yet moist pastries and to prepare the lightest soufflés. In many cases they follow long-winded and complex (but well-tried and -tested) procedures to achieve their desired results. However, often, with a little understanding of the underlying stability criteria, they can achieve the same result with far less trouble. A glance at any cookbook on how to produce a simple mayonnaise shows that many cooks do not have even a basic grasp of thermodynamics of emulsification.

However, there is much more to explore here than elucidating what makes those things chefs already do work (or fail). The understanding of physical chemistry to control texture in, for example, emulsions, gels, foams, and glasses has an enormous range of potential applications to produce foods of novel and interesting textures in the kitchen.

This is an area where there has already been a good deal of transfer of knowledge from the science laboratory into the kitchen ("spherification" using calcium to mediate gelation of alginate systems^{200,201} foams that hold and release specific flavors in a controlled way, hot jellies,⁶² etc.).

Our aims in this section are first to explain the physics and chemistry involved in the development of specific textures in traditional cooking processes (e.g., in roasting or frying meat, baking a cake, etc.) and second how we can use our understanding of thermodynamics and materials science to provide different ways to control texture in the restaurant and domestic kitchen.

We have chosen to divide the section into two parts. In the first part we will look at how best we can describe the texture of a wide variety of processed foods (breads, cakes, ice creams, and so on) with a view to providing a physical chemical background to the production and stability of such processed foods. In the second part we will look at the texture of naturally occurring foods (in particular meats) and how these textures can be changed by cooking.

4.3.1. Relationships between Perceived Texture and Measurable Physical Properties

At first sight it would appear that it ought to be a simple matter to relate the perceived texture of food in the mouth with measurable physical properties of the food (for example, tensile and shear modulus and fracture stress for solid foods and viscosity for liquids). However, as with all things matters are far from this simple. First, very few if any foods have mechanical properties that can be characterized by single-valued properties. Foods are complex substances and have correspondingly complex physical properties. They are at best viscoelastic, so that knowledge of properties over a wide frequency domain would be necessary before any relationship between perceived texture and measurement is possible. However, most foods display distinct nonlinear properties, making the problem much greater. To complicate matters further, as we chew the food in the mouth it interacts with saliva and changes its properties, leading to changes with time that are more or less impossible to simulate in the laboratory. Worse still, everyone will chew their food differently, so that the perceptions they have will differ. Consider, for example, a food that is distinctly nonlinear, one that has a very low modulus and shear strength at low frequency and small amplitude but which at higher frequencies and amplitudes becomes a rigid solid with a high shear strength. Such a food might seem soft and smooth to a person who chews slowly but hard and brittle to somebody in a rush to eat their food. Accordingly, successful attempts to relate perceived texture to measurable physical properties are few and generally limited to specific types of food and textural descriptions.

The best documented cases of direct relationships between measurable physical properties and perceived texture lie in the area of "semi-solid" foods such as yogurts and custards. The perceived thickness, T , of such foods can be modeled in terms of the shear stress, σ , "felt" on the tongue as the food is consumed. Several authors (e.g., Kokini^{202,203}) have

reported a relationship of the form $T = a \cdot \sigma^b$, where a and b are constants that depend both on the food being consumed and on the method by which perceived thickness is evaluated by the taste panels. The shear stress felt by the tongue has itself to be calculated from a knowledge of the viscosity of the food; again, there are different models to do this (see, for example, the fluid mechanical calculations of DeMartine and Cussler²⁰⁴). Terpstra et al.²⁰⁵ provided a detailed discussion of these models together with some comments on their limitations.

Although it is difficult to provide clear predictive relationships between measured physical properties and perceived texture in the mouth, textural measurements remain useful for food scientists developing new products, if only to permit elimination of products that are likely to prove to have unpleasant textures or as quality control techniques. In both cases, it is possible to create specific measurements that can be used to select products that may need further testing.

The range of texture-measuring methods that have been devised over the years reflects on the ingenuity of those working in the field. All manner of devices have been constructed to simulate what happens as we eat our food, from the simplest of measurements of stiffness and failure stress using standard testing machines to a specially designed and built apparatus that simulates the movement of jaws and teeth as we eat.²⁰⁶⁻²⁰⁹

4.3.2. Complex Nontissue Foods: Foams and Emulsions

The texture of (solid-like) foods varies from incredibly light and soft foams to very hard and brittle boiled sugars. The range of possibilities is so vast that it is not possible to list them all. In this section we first outline the wide range of possible microstructures that occur in the world of foods and catalog them as foams, emulsions, and colloids or more complex multiphase materials. At the same time we try to show how the different microstructures relate to the physics properties of these foods.

Very few foods and food ingredients can be characterized as being a single phase. Examples include water and simple solutions. Aqueous solutions include naturally occurring ingredients such as egg whites (which can be thought of as a 10% aqueous solution of the proteins ovalbumin, ovotransferrin, ovomucoid, globulins, lysozyme, ovomucin, and avidin as well as small amounts of salts and carbohydrates) and red and white wines where the major solute is ethanol, although it is the other minor solutes such as tartaric acid, flavanoids, tannins, and aldehydes that provide the wine's flavor. The various oils used in cooking are nominally mixtures of various liquid triglycerides. Olive oil, for example, is mainly composed of a mixture of four triglycerides composed of oleic acid, O, lauric acid, L, and palmitic acid, P; these may be referred to as OOO (three oleic acids joined together), LOO (one lauric acid together with two oleic acids), POO, and SOO. These triglycerides further act as a solvating medium for various minor components: short-chain alcohols, chlorophylls, fat-soluble vitamins, etc. Sugar and salt are the most common single-phase solid ingredients used in the kitchen. Sugar can, as we shall see later, be heated to a liquid phase and then spun and cooled quickly to form a glass: examples of spun glass foods include candy floss. Glassy sugars can also act as solvents in the case of hard candy. Such products, in their simplest versions, are single-phase materials where colorants and flavor molecules are dissolved in amorphous sugar.

Table 4. Examples To Illustrate the Multiphase Nature of Foods^a

one phase	
wine, oils, hard candy, noncarbonized soft drinks	
two phases	
vinaigrette dressing	oil and aqueous phase
slush ice	crystalline water and aqueous phase
whipped egg white	air and aqueous phase
mayonnaise	oil and aqueous phase
beer foam	air and aqueous phase
three phases	
butter	crystalline and liquid fat and aqueous phase
dark chocolate	crystalline fat, crystalline sucrose, cocoa solids
four phases	
parfait ice cream	aqueous phase, fat, air, crystalline water
milk chocolate	crystalline fat, liquid fat, crystalline sucrose, cocoa solids
five phases	
butter cream	crystalline fat, liquid fat, crystalline sugar, aqueous phase and air
six phases	
fudge	crystalline sugar, aqueous sugar solution, air, liquid fat, crystalline fat and cocoa solids

^aThese examples are simplified as some phases can in reality be expanded into more phases (e.g., crystalline fat really consists of several crystalline phases).

While it is possible to find a number of examples of single-phase foods, the vast majority of the materials in the world of foods are of multiphase nature. Simply moving from a still white wine to a sparkling wine such as champagne immediately doubles the number of phases. Champagne, when in the bottle, may be considered as a pressurized, supersaturated solution of carbon dioxide. As soon as it is served it is better considered as an unstable dispersion of rapidly nucleating carbon dioxide bubbles. These bubbles constitute the second phase of the material. Table 4 shows examples for the development of the complexity of food materials.

Most foods can be described in terms of a number of dispersed phases, surrounded by a continuous phase or matrix. Such systems are, in general, termed colloids, and depending on the properties of the continuous and dispersed phases they can be classified into the categories solid sols, solid foams, sols, emulsions, foams, solid aerosols, and liquid aerosols.

Not all of these colloidal states are equally important in foods and cookery. A liquid dispersed into a gas is called a liquid aerosol. We do not know of any examples of dishes or foods with this type of structure. Nevertheless, if one sprays a liquid on some food, an intermediate mist-like material is produced, which indeed is a liquid phase that is dispersed into a gas phase. The smoke used for smoking foods belongs to the category of solid aerosols: solid particles dispersed in a gas phase.

Moving to combinations that are found commonly in foods, we begin with the case of a solid dispersed into a liquid. Such systems are termed sols; examples include melted chocolate, chocolate sauce, and cold cream (where the fat particles are cool enough to be solid). Sols are mostly used in cooking as sauces and some soups; the important properties for the chef are the “thickness” and “creaminess”.

In general, a more viscous liquid matrix and a higher concentration of solid particles will increase the “thickness” of a sol-based sauce, while higher proportions of small particles will tend to increase its creaminess.

A solid phase dispersed into another solid phase constitutes a solid sol. Dark chocolate is an example of a solid sol as both the two solids, sugar and cocoa powder, are dispersed into the continuous solid fat phase. In the case of solid foods chefs tend to be concerned about whether they are tough, brittle, hard, or soft. Generally, in systems where one or more solid phases are dispersed in a single matrix, the properties of the matrix dominate, so if the matrix has a high tensile modulus the product will be perceived as hard if it is ductile, with a low yield stress, as soft, and so on. However, the size and concentration of the solid inclusions also affect the perception of the overall properties in the mouth, especially if the inclusions are macroscopic so they are felt by the teeth (or tongue) as the food is eaten.

A gas dispersed into a solid matrix is called a solid foam. The range of properties that can be achieved with solid foams is vast; the properties of the foam relate mainly to the properties of the solid matrix. At one extreme are the brittle foams that melt in the mouth; these can be light and delicate (such as dry meringues) or hard and brittle (the foamed chocolate “Aero” bars). At the other extreme are the ductile foams that produce, for example, sponge cakes. Stiff matrices with a high-yield stress provide hard or tough foams (e.g., stale and toasted breads), while low-modulus matrices with low-yield stress tend to provide softer weaker foams (e.g., light sponge cakes); brittle matrices produce foams that burst open when bitten into (e.g., dry meringues), while ductile matrices produce foams that melt in the mouth as they are chewed. While the matrix properties dominate the general character of the product (hard, soft, brittle, etc.), the size and proportion of the dispersed bubbles determine how “light” the product is perceived, more small bubbles tending to produce a “lighter” result.

When a gas phase is dispersed into a liquid phase it produces foam. Foams are very common in cookery, both as an intermediate step to a product (bread dough may be considered a foam prior to cooking), as a part of a dish (the whipped cream on top of the strawberries), or even a complete dish in its own right (soufflés). The key properties of foams, from the point of view of the cook, are similar to those of sols. Foams are interesting low-viscosity fluids, air is dispersed, often in high volume fraction into a fluid of higher viscosity. The material formed by the two phases; the foam can behave as a solid (a bowl containing beaten egg whites can often be turned upside down). However, if we consider its nonlinear rheological behavior then foams are better described as plastic materials that can be permanently deformed beyond the yield stress limit. The yield stress as well as the static shear modulus depends on interfacial tension, the average bubble radius, and the volume fraction of air; a theoretical expression yield in foams has been derived by Princen and Kiss.^{210,211} Emulsions are formed when a liquid phase is dispersed into another liquid phase. Emulsions constitute perhaps the largest group of food colloids. In gastronomy most sauces and dressings fall in this category.

The key properties of the sauces for the chef are “thickness”, “creaminess”, and “stability”. The first two generally follow those of the matrix, but in some cases (e.g., mayonnaises) the properties of the product can be very different

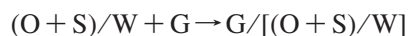
Table 5. Some Illustrative Examples of the Use of the Classification Schema of This

food	This classification	description
cream	(O + S)/W	suspension of liquid and solid fat particles in an aqueous solution
whipped cream	G/[(O + S)/W]	gas bubbles trapped in a suspension of liquid and solid fat particles in an aqueous solution
egg custard	(G + O + S)/W	liquid fat drops, solid particles (from cooked proteins), and gas bubbles (from air trapped during beating of the custard) all suspended in an aqueous solution
sponge cake	G/S	air bubbles in a solid matrix
egg yolks	(S/W) ⁹	nine concentric layers each made up of solids suspended in an aqueous solution; the example illustrates how the classification can be used to provide information about inclusions within the various phases
specific emulsion	O ₁₀₀ /W ₁₀	emulsion of 100 g of oil in 10 g of water; the example illustrates how the classification can be made quantitative

from those of either component. The third, stability, is far more complex and deserves a section on its own.

Hervé This⁸ recently attempted to provide a schema to classify the wide variety of possible structures in foods. To do this he considers four basic “phases”: gaseous phases (G), normally simply air but including any gaseous phase, for example, steam or alcohol vapor; liquid aqueous phases (W), pure water or any aqueous solution irrespective of the type or amount of solutes; liquid oil-based phases (O), any oil, mixture of oils, or solutions of molecules of any type in oils (an oil is taken to be any lipophilic liquid); and any solid phases (S) no matter what their chemical composition or internal structure, including solid fats, ice, carbohydrates, etc.

Having thus defined four basic continuous phases from which all foods can be made, This suggests that we may consider the structure of foods in terms of how these are arranged and provides a formalism to permit a concise description of the internal structure of a foodstuff. For example, cream (a mixture of solid and oily liquid particles in a continuous aqueous phase) would be described as (O + S)/W, the “/” symbol indicating the oil (O) and solid (S) inclusions are contained within a continuous aqueous phase (W). Whipped cream occurs when gas bubbles are incorporated into the cream, so it would have structural code G/[(O + S)/W]. This further suggests that such symbolism can be used to describe the transformations that occur in kitchen operations, so the production of whipped cream could be represented by the equation



Further, with the use of superscripts and subscripts it is possible to include information about the sizes (or range of sizes) of the various phases and denote complex cases where already multiphasic inclusions are contained within one another, building up complex hierarchical structures. We show in Table 5 a few examples of how particular foods can be classified in the This schema.

The utility of such a classification is that it can be used to see the generality of the various types of products used in the kitchen. For example, This carefully analyzed all the classical French sauces according to this schema and found that just 23 categories have been used.⁸ More interestingly, he found that some simple types have not been used by traditional French chefs. The simplest sauce not used in

traditional French cuisine is G/W (bubbles in a liquid). Many gastronomic restaurants now use such foams in a wide range of sweet and savory dishes. While such developments were not directly inspired by the This schema, it is possible that future generations of chefs may find novel dishes and variations on existing dishes by examining such classifications.

4.3.2.1. Stability of Food Colloids. From a thermodynamic point of view, more or less all emulsions and food colloids are unstable. That is, the free energy of food is higher in the emulsion or colloidal state than it would be if the food were to separate fully into two (or more) macroscopic regions. For example, a simple *vinaigrette dressing* will, given time, separate to form two completely separate regions of oil and vinegar; the dressing is only temporarily mixed into an emulsion when the oil and water are shaken together and demixes spontaneously once the agitation stops.

The excess free energy of an emulsion is created by the internal interface area of the system. The excess Gibbs free energy of creating a surface of area, dA, can be written as $dG = \gamma(dA)$, where γ is the surface free energy density or the surface tension $\gamma = ((\partial G)/(\partial A))_{T,p}$. The surface tension is always positive (a hypothetical negative surface tension would cause an unstable and spontaneously growing surface). Since colloids are systems of excess surface area, as compared to the macroscopically phase-separated systems, the dispersed situation is always going to be thermodynamically unstable. However, it is possible to construct colloids so that they lie at local (rather than global) minima of the free energy and so are at least metastable.

While preparing an emulsion, foam, or other colloidal dispersion, a surface has to be formed. The work needed to create the surfaces in emulsions and foams is $w = \gamma\Delta A$, where ΔA is the excess area created. While a chef might not be fully aware of the thermodynamics of emulsions and foams, he or she will fully acknowledge the work needed for stirring, whipping, and beating the food materials. Often powerful kitchen machines are used to obtain the right degree of dispersion.

A simple example serves to illustrate the power needed to achieve an oil–water emulsion. For a hypothetical oil in water emulsion with a volume fraction of 0.1 and droplet size of 0.30 μm the surface area is $2 \times 10^3 \text{ m}^2/\text{L}$. A typical value of the triacylglycerol water surface tension is 30 mN m^{-1} , so that the resulting excess free energy (or work needed) is 60 J/L. Thus, to make a liter of such an emulsion at least 60 J of work needs to be done on the mixture. However, since the emulsion is inherently unstable, the work needs to be applied in a short time, less than the “relaxation time” of the droplets, which will typically be significantly less than a second. Thus, any mixing device used to create emulsions needs to have a power in the region of hundreds of Watts and to run at high speeds to induce the high shear strain necessary both to deform the phase to be dispersed and to break it into droplets. Examples of such industrial devices include rotor stator types with narrow slits and high-pressure homogenizers using large pressure drops and those that force the liquid through a narrow slit at high velocity. Neither of these will, on their own, create an emulsion; they simply disperse an existing emulsion into finer droplets. As yet we are not aware of any purpose built equipment for the domestic kitchen designed to create emulsions. Rather, chefs and cooks tend to use inefficient methods such as manual whisking, where most of the energy is “wasted” going into

viscous heating of the liquids rather than into the creation of (and reduction in size of existing) droplets.

4.3.2.2. Kinetics/Dynamics of Degradation of Structure.

The stability of a structure can be characterized by a lifetime before severe degradation (in this case before macroscopic phase separation becomes apparent to the diner). This lifetime should be compared with other relevant time scales for the product, such as those for chemical degradation, microbiological contamination, and consumption.

Knowledge and empirical understanding of stability have become built into traditional recipes and procedures; indeed, recipes for many sauces have evolved so that the sauce remains stable long enough to be taken from the kitchen to the table and consumed over a prolonged period. However, when chefs develop novel dishes they have to address the various questions of colloidal stability to ensure the product remains stable from the time it is completed in the kitchen to the time it is finally consumed in the dining room. To this end they must select the appropriate ingredients and stabilizing additives. Further, they need at least an empirical understanding of the conditions under which the structure will remain stable and how long it will remain sufficiently stable. In some cases longer time scales become important. Mayonnaise, if well prepared, has a lifetime of much longer than the time between manufacture and serving, so a more relevant time scale to consider is that of chemical or microbiological degradation.

4.3.2.3. Mechanisms/Processes That Result in Phase Separation or Severe Degradation of Structure. The field of liquid–liquid phase separation is well studied and understood in terms of the underlying thermodynamic drivers. Accordingly, the stability of sols and emulsions is perhaps best viewed in terms of the various mechanisms of phase separation.

4.3.2.3.1. Sedimentation/Creaming. In the food industry the process of “creaming” in emulsions is well understood. Essentially, provided the droplets are large enough that Brownian motion is not sufficient on its own to keep them suspended, the droplets will slowly diffuse either upwards or downwards due to the density difference between the two phases. This is what happens to whole milk when left to stand—the cream rises slowly to the top.

The simplest approach is to find the steady-state drift speed of dispersed droplets assuming spherical droplets and frictional forces obeying Stoke’s equation,

$$v_s = \frac{g(\rho_D - \rho_C)d^2}{18\eta_C}$$

where d is the droplet diameter, ρ_D and ρ_C are the densities of the dispersed and continuous phases, and η_C is the viscosity of the continuous phase.²¹² Stoke’s equation is rarely used quantitatively as several additional effects lead to deviations from this simple estimate of drift velocity; nevertheless, it can provide some guidance and insights for the improvement of the stability of colloids and emulsions in the kitchen.

If the drift velocity can be reduced, the stability will be increased. The simplest approach is to reduce the particle size; reducing the particle size by a factor of 10 will lead to a 100-fold reduction in drift velocity and correspondingly increased stability. The simple rule of thumb for chefs is that smaller droplets (generally made by doing more work) will produce more stable sauces.

One method to reduce droplet size is that used commercially in the homogenization process of milk.²¹² Fat

droplets in raw milk have a fairly broad size distribution, ranging approximately from 1 to 7 μm .²¹³ After a typical homogenization process at 20 MPa, the distribution is quite narrow and typically peaks at 0.25 μm . Gastronomic and domestic kitchens might benefit from similar machinery for efficient homogenization.

Alternatively, the stability of such systems can be manipulated by controlling the viscosity of the continuous phase perhaps by adding thickening agents (such as the starches used to thicken some sauces; or the use of sodium carboxymethyl cellulose, locust bean gum, etc. in some commercial products). Using such additives, the viscosity and thereby the colloidal stability can, in many cases, be improved a few orders of magnitude.

4.3.2.3.2. Aggregation and Coalescence. As well as droplets separating under gravity, they can aggregate into usually undesirable structures of larger size, which then, due to their increased size, may be subject to enhanced rates of sedimentation/creaming.

On the most basic level, aggregation can be described through Smoluchowski theory,^{214,215} which emphasizes the rate of the process as being diffusion limited. However, the theory does not include the rather important effect of repulsive forces between particles and thus underestimates the stability of food dispersions.

Coalescence is a small step further and results in the complete fusion of two or more particles. For example, in the case of a vinegar/oil dressing, coalescence typically takes place once the droplets become closely packed together, having gained a high concentration (either at the top or bottom of the container) through the sedimentation/creaming process. In beer foams, a large quantity of the liquid phase drains back into the beer under gravity and the air bubbles coalesce in to a coarser structure, which eventually collapses.

Partial coalescence is an intermediate between complete fusion and aggregation. In whipped cream the fat globules reach a partial coalesced state and act to form a solid-like network that gives the whipped cream its physical stability.^{216,217}

There is little the chef can do to prevent aggregation and coalescence except to be aware that they will happen and will generally happen more rapidly where the droplets are closer together and where the surrounding medium is less viscous. But it is worth noting the importance of electronic repulsion between like charged droplets—this is often the main stabilizing effect where the droplets become charged—increasing the charge on the droplets (usually by more and harder beating) can significantly affect stability—as every chef knows from experience making mayonnaise.

4.3.2.3.3. Ostwald Ripening. Ostwald ripening is due to diffusion of individual molecules through the continuous phase from smaller, less stable droplets to larger droplets. The process is driven by the destabilizing surface contribution to the free energy that makes the chemical potential larger for migrants present in the small particles as compared to larger particles. This effect creates concentration gradients of the migrant in the continuous phase and thus a net diffusion. Ostwald ripening is well understood and has been observed in a wide range of phase-separating systems.

In particular, Ostwald ripening provides for fast growth of the dispersed phase if it is highly soluble in the continuous phase. The process, therefore, is slow for dressings such as water-in-oil emulsions. However, it can be very fast in the case of beer foam since carbon dioxide is highly soluble in the aqueous phase. The mechanism also becomes relevant for

Table 6. Some Commonly Used Ingredients That Contain Significant Amounts of Emulsifiers

ingredient	key emulsifier component
egg yolk	phospholipid (lecithin)
egg white	globular proteins
whey powder	whey proteins
milk powder	caseins and whey proteins
soy bean	phospholipids and proteins
mustard seed (especially yellow mustard)	mustard mucilage, a gum of mainly polysaccharide origin acts as a shear-thinning thickener and possibly as an emulsifier ²¹⁹
flax seed	flax seed mucilage, polysaccharides, which act as shear-thinning thickeners ²²⁰

products that are stored for long times, such as commercially produced frozen desserts. In such cases, the phenomenon can result in large ice crystals and unpleasant textures.²¹⁸

In systems where one phase is partially soluble in the other, small fluctuations in temperature (or pressure) will cause changes in the amount of the dispersed phase as a new equilibrium partition is reached. When the external factors return to the original state and the net amount of dispersed phase is restored, the size distribution of particle will change toward larger sizes. The phenomenon can be seen as an enhancement of the Ostwald ripening process. This sort of process is particularly important for storage of frozen desserts as temperature fluctuation in freezers can lead to the irreversible growth of large ice crystals.

To conclude, while chefs have some tools available to combat phase-separation processes that inevitably destabilize the product they make, it is never possible to eliminate the tendency of small droplets of dispersed phases from growing larger over time. All that we can do is to be aware of the time scales involved and make sure that products remain sufficiently stable over a long enough period that the diner can enjoy them to the fullest extent possible. It is perhaps for this reason that it can be particularly challenging to transfer the gastronomic dishes prepared in restaurants to the wider food industry. In a restaurant environment, it is possible to produce and serve dishes that have a lifetime of minutes, while the commercial retail industry demands products with lifetimes in the region of days or even months.

To provide such long lifetimes it is often necessary to introduce additional “stabilizing” compounds. These stabilizers in turn introduce their own tastes and textures, which often change the character of the original dishes, often making them less attractive. However, as we shall see in the gels section, some chefs are now starting to use some of these “stabilizers” and use them to enhance the range of gastronomic dishes they prepare. So there is some hope that in the future with superb creative chefs regularly using the types of food additives that were seen as only fit for “processed” foods a few years ago, we may soon see gastronomic quality foods appearing on the supermarket shelves.

4.3.2.4. Ingredients and Compounds That Enhance Colloidal Stability. There is a wide range of food molecules which can be used to increase the stability of foams, sols, and emulsions. Generally, these molecules are grouped into two categories: emulsifiers and surfactants as well as stabilizers. They are widely present in food ingredients. Typical examples include polar lipids (monoglycerides, diglycerides, phospholipids, glycolipids, etc.) and globular proteins (such as beta-lacto-globulin); some common food examples are given in Table 6. These molecules tend to reduce the surface tension between the phases. The reduced

Table 7. Some Stabilized Systems and the Stabilizers Present

food	stabilizer
mayonnaise, hollandaise, béarnaise	egg yolk lecithin
vinaigrette	can be stabilized by mustard
beer foam	range of proteins from barley that are more or less degraded during boiling and brewing
cappuccino foam	casein and whey proteins of milk
espresso foam (the crema)	foam stabilized by surface active compounds of polymeric nature (proteins, melanoidins, and polysaccharides) formed during roasting of coffee ²²¹
bread crumb	complex foam stabilized by among others gluten, before baking, and a solid starch network of the cold crumb after baking
whipped cream	stabilized by surface active phospholipids and mechanically by partial coalescence of fat globules of the cream

excess surface energy decreases the driving force for phase separation. This affects both the ease of formation of emulsions and the stability of the final preparation.

The presence of an emulsifier decreases the work associated with deforming and breaking up larger droplets into smaller ones. This usually results in a size distribution shifted to smaller sizes, and thus, the rate of the creaming/sedimentation process is lowered. The kinetics of the phase separation process into bulk phases is also modified by the presence of surface active components. The lowering of the surface tension also lowers the concentration/pressure differences responsible for the Ostwald ripening.

The accumulation of surfactant at the internal surfaces of the food colloidal will also in most cases modify the forces acting between the dispersed particles. Most prominent is the accumulation of charged surfactant, which gives rise to long-range electrostatic repulsion between dispersed particles and thus a kinetic stabilization against aggregation phenomena. In Table 7 we listed some examples of prepared foods which are stabilized using such molecules together with the stabilizers used.

In restaurant and domestic cooking food needs only to be stable long enough to go from the kitchen to the table and be consumed. Thus, it is possible to prepare and use foods that are in a metastable and even an unstable state. An interesting example, from the Fat Duck, is that of a green tea foam palate cleanser (for a recipe and photograph see page 133 of *The Big Fat Duck Cookbook*⁶²). The basic concept arose once it was noted that a mixture of green tea and vodka in an egg white foam acts as an excellent palate cleanser. Being a foam which disappears quickly it can be served right at the start of a meal with no risk of spoiling the appetite as might a larger more dense version of the same ingredients. However, there is a problem of stability: the foam very quickly collapses, leaving some liquid at the bottom of the glass in which it is served. Thus, it has to be prepared right at the table and consumed immediately. However, not everyone is cooperative; some people will leave it to stand (perhaps to savor it), but the stability is insufficient. In the end a solution was found by freezing the

foam in liquid nitrogen to make a small “poached” hard-shelled meringue-like sphere that can be put in the mouth where it instantly disappears, cleaning the palate.

4.3.3. Crystalline State in Foods

Many of the ingredients we use in our kitchens are fully or partly crystalline materials (examples include sugars, fats, many carbohydrates, and salt). During the preparation of the food these materials will often pass through other liquid or amorphous states due to action of heat or solvents such as water. Eventually the original ingredients may, through solvent removal during baking and cooking and by cooling after heat treatment, be turned into new materials which in many cases also involve (new) crystalline structures. Often multiple competing crystalline forms can coexist. The recrystallization from one metastable form into a more thermodynamically stable form is part of the (usually undesired) aging of food. Overall, an understanding of these phase transitions of food ingredients can enable the chef to obtain a wide range of textures using the right combination of ingredients, heating, and drying.

4.3.3.1. Water. Of all the food molecules that occur in crystalline form, water is the most common. Ice is used in many desserts such as ice creams and sorbets. Ice is also present in all frozen foods, and so the growth of ice crystals is important in considering their long-term storage.

In sorbets and ice creams it is important that there is a liquid phase present to provide enough fluidity to make the dish soft and easy to eat. With no liquid phase the ice would remain hard and unpleasant. This is achieved through the addition of sucrose, other sugars, or other solutes such as ethanol to create a sufficient freezing point depression to leave a substantial portion of unfrozen aqueous solution at the typical serving temperature from -13 to -6 °C and even at conventional storage temperatures from -15 to -20 °C. In many ice creams the sugar content is as high as 15%, somewhat higher than the typical sugar content of other desserts. However, at the low temperatures we become less sensitive to the sweet taste.

Some frozen desserts such as granites are made with only limited amounts of sugar or other solutes, and the final snowy texture of such dishes relies on mechanical treatment of the initially rather solid and hard ice. Recently, novel blenders for use with frozen foods (such as the Paco Jet, see later, section 4.4.2.5) have been exploited in restaurants to make finely dispersed ice particles and expanded the range of possibilities within frozen desserts.

When considering the storage of frozen foods we need to note first that the initial freezing creates ice crystals that can damage the texture of the food being frozen, so that it is usually best to freeze as quickly as possible to create the smallest possible crystals. We discuss how crystallization temperatures and rates affect crystal sizes later. Second, it is important to realize that these small ice crystals are not thermodynamically stable. Larger crystals will grow larger at the expense of smaller crystals that will disappear in a process comparable to that of Ostwald ripening described previously. Such recrystallization is also promoted by the presence of a liquid phase. In most foods there are some salts and sugars present in the aqueous phase. On freezing, as ice forms, so the concentration of the sugars and salts increases, but since the eutectic temperatures of most salt mixtures are below those found in most domestic freezers, some aqueous solution usually remains in the frozen foods.

4.3.3.2. Carbohydrates. Simple sugars are generally refined into crystalline powders and granules of high chemical purity. These are essentially single-component materials so that, in principle, they possess sharp, well-defined thermodynamic melting transitions. However, most sugars are not chemically stable; they undergo dehydration reactions upon heating, which affect the melting behavior. These caramelization reactions have been discussed previously. There are a number of dishes (such as the *crème brûlée*) where the flavors and color of the caramelization reactions are desirable. However, it is also often the case that chefs may wish to produce sugar products that do not have the caramelized taste or color but which nonetheless need to be heated; examples include spun sugars and candy flosses.

Two solutions are possible. First, it is possible to select sugars that are more stable; there are some sugars, in particular, the sugar alcohols, xylitol, sorbitol, and maltitol, which are stable against dehydration reactions and can be melted without any significant browning. Second, mixtures of different sugars can be used so as to reduce the melting temperature range.

For example, boiled sweets are based on a combination of sucrose and glucose (in some countries glucose syrups). The preparation involves boiling the solution at an increasing temperature (the temperature rises as water boils off due to pronounced boiling point elevation of the highly concentrated solutions). The process is stopped at a temperature of about 146 – 154 °C, indicating a very low water content. However, due to the presence of two or more sugars (or glucose oligomers) as well removal of most of the water, crystallization of sucrose and glucose on subsequent cooling is kinetically suppressed,²²² so that the process directly provides a supercooled (glassy) sugar melt without entering the high-temperature regions used to melt sugars that accelerate the dehydration reaction of sugar. The effect of glucose, glucose oligo- or polymers on the crystallization of sucrose has been systematically studied by differential scanning calorimetry.²²³

As we shall see later, sugars can also be quenched to form glassy materials. Crystalline sugars are desirable in many dishes and products (including chocolate, fondant, fudge, dry meringues), while glassy sugars are required in other dishes (such as hard boiled candy). The presence of crystalline sugars not only contributes to a sweet taste but also changes the texture of the product depending on the amount and size distribution of the crystals. Some sugars, mainly xylitol and to some extent sorbitol, dissolve quickly in water through a strongly endothermic process and can be used to create a cold sensation in the mouth.

As we shall see in detail in the gels section starches are present in many basic ingredients such as flour and potatoes, etc., in the form of small, partly crystalline, micrometer-sized starch granules. The crystalline parts consist mainly of the macromolecules amylopectin and amylose. Due to the action of a combination of water and heat the crystalline parts of the granules will melt and the granule will take up water and swell; eventually the whole granule can disintegrate. The process is called starch gelatinization. The melting of the crystalline regions occurs at increasingly high temperatures with decreasing water content.²²⁴ The melting temperature reaches its lowest level (about 58 °C in the case of potato starch) independent of water content if excess water is present.²²⁵

4.3.3.3. Fats and Oils: Triglycerides. Fats and oils are multicomponent materials with a multitude of crystal phases

that can all coexist, making their crystallization and melting behavior significantly more complex than simple systems such as the sugars. Mixtures of triglycerides in a liquid state are normally called oils, whereas purely or mainly crystalline triglycerides mixtures are called fats. Triglycerides show a richness in polymorphic forms, which can be grouped into three main types, α , β' , and β . Thermodynamically these polymorphs are distinguished by increasing stability (decreasing free energy) and increasing melting point in the order α , β' , and β . On a structural level, they differ in the methylene group packing arrangements as seen by wide angle X-ray diffraction experiments.²²⁶

The sizes of individual crystallites are typically a few micrometers. In fats with a content of liquid triglycerides, the crystals of fat can form a network that penetrates the materials, making a gel-like system with plastic deformability, giving rise to the well-known texture and spreadability of ingredients such as butter, margarine, and pork fat. For most fat types metastable crystals of β' type give rise to the most optimal crystal size distribution and crystal network and are therefore desired in ingredients such as butter, margarine, and some forms of chocolate. A culturally based exception to this is the middle eastern ingredient, butter ghee (a butter fat without water and proteins), where a grainy texture based on β crystals is preferred.

Phase diagrams of some triglyceride mixtures have been determined.^{227,228} However, in general fats can be considered to be multicomponent mixtures as well as multiphase materials. For such complex systems the derivation of complete composition temperature phase diagrams is almost impossible. Instead, for a specific fat or combination of triglycerides the SFI (solid fraction index), the fraction of crystalline material present, can be derived as a function of temperature using techniques such as DSC or low-field nuclear magnetic resonance spectroscopy (NMR).²²⁹ In such studies the detailed connection between the underlying phase behavior and the SFI-melting profile remains unclear. However, it is clear that the incompatibility between crystals of different triglycerides can lead to eutectic-like phenomena. The number of phases present is comparable to the number of different triglycerides, which for most fats can be large (>10), making the detailed materials science of fats extremely complex. In general, all that can be said is that they usually have very broad melting ranges.

However, in some systems with fewer triglycerides and where they have compositions that lie close to the eutectic-like proportions a comparatively sharp melting temperature can be seen. Cocoa butter, a chemically simple fat, has three major components: POS, POP, and SOS (using the notation defined in section 4.3.2). When cocoa butter is in the so-called state V, a β' polymorph (the desired polymorph for chocolate), it has a melting temperature just below body temperature. This form of cocoa butter lies close to the eutectic composition for the tempered system of the three triglycerides POS, POP, and SOS, explaining the sharpness of the melting process of dark chocolate. The much broader melting interval of butter and pork fat can be understood in this context in terms of a triglyceride composition further way from the eutectic composition of the relevant triglycerides.

Finally, we should mention that the presence of metastable polymorphs further complicates the measurement and observation of phase behavior since the melting behavior becomes strongly dependent on the thermal history. For example, it is often found that parts of a material will

crystallize and release heat upon heating. Unstable polymorphs melt at relatively low temperatures on heating (for example, in a differential scanning calorimeter (DSC)) to form supercooled melts which subsequently crystallize into more stable polymorphs and finally melt again.²³⁰

4.3.3.4. Nucleation, Growth, and Other Dynamic Aspects of Crystalline Phases in Gastronomy. One of the most important issues with crystalline food systems is the size of the individual crystals. The overall crystallization rate and distribution of crystal sizes are determined by the rates of both nucleation of new crystals and growth of existing crystals. Both rates increase with the thermodynamic driving force (which depends, inter alia, on the supercooling or supersaturation), and both decrease as the mobility of the molecules decreases. The result is usually a bell-shaped curve for the rates as a function of, i.e., temperature, with rates at first increasing and then passing through a maximum before decreasing as the temperature is lowered. However, the relative rate of nucleation to that of growth tends to increase as the thermodynamic driving force increases, leading to significantly smaller crystals being formed at the highest supercoolings (and for crystallization from solution the highest supersaturations).

Implicit qualitative knowledge is often inherent to classical gastronomic procedures. In the making of fondants and chocolate, often the hot sugar melt/solution or parts of the melted chocolate are poured on to and kneaded on top of a marble block, which ensures fast cooling and with it formation of very small crystals. When making ice cream the ice cream mix is usually stirred vigorously while being cooled in order to maximize the supercooling and break up any large crystals that may grow to produce a very fine dispersion of ice crystals, which is very important to the perceived texture of this frozen dessert. Dry meringues are baked for a long time at sufficiently low temperature (≤ 105 °C, well below the melting point, ca. 185 °C, of sucrose) in order to ensure that sucrose will crystallize as the water is removed.

In cases where prevention of crystallization is desired, as in the making of hard-boiled sweets, we exploit the fact that crystallization can be quenched by sufficiently fast cooling through the temperature interval of overall fast crystallization and into a more kinetically stable temperature region. However, it should be noted that crystallization of such impure material must involve accumulation of impurities and diffusion over increasingly longer distances as crystallization progresses (rather than forming a supersaturated/supercooled melt that eventually will be glassy).

4.3.4. Glassy State in Foods

Some of the macrocomponents of food, such as sugars, larger carbohydrates, and to some extent proteins, form glasses when melts or solutions of these food components are cooled or dried sufficiently fast to avoid the crystallization processes. Glass formation is important for the description and understanding of hard-boiled candy, candy floss, cookies, crusts, and crackers, etc. In fact, more or less all crunchy or crisp foods are in a glassy state.

Briefly, a glass is, from a structural point of view, a molecularly disordered material that behaves from a simple mechanical point of view as a solid, characterized by a high shear modulus of the order of 10^{12} Pa. However, food glasses are often more like very viscoelastic liquids which show very slow relaxation processes (with relaxation times, τ , of many

Table 8. Calorimetrically Determined Onset Glass Transition Temperature of Various Dry Food Components

component	$T_g/^\circ\text{C}$
xylitol	-29
sorbitol	-9
fructose	5
glucose	31
sucrose	62
trehalose	110
lactose	101
nonsugars	
water	-133
starch	243
gelatin	100

hours) and can thus also formally be assigned a viscosity $> 10^{12}$ Pa s. Glasses are also brittle, which is very important for the perceived crunchy textures they produce.

The rates of the relaxation processes as well the viscosity of food glasses are heavily dependent on temperature with a strongly non-Arrhenius temperature dependency. When cooling amorphous food materials, the very steep dependency on temperature gives rise to a moderately well-defined transition from liquid behavior to solid behavior at the so-called glass transition temperature, T_g . Differential scanning calorimetry using standardized scanning rates of 5–10 deg/min is the preferred technique for the determination of glass transition temperatures in food systems, although other methods can be employed.²³¹

The strong temperature dependence of the viscosity near the glass transition is most commonly described by the Williams–Landell–Ferry expression (the WLF equation):

$$\ln(\eta(T))/(\eta(T_0)) = (-C_1(T - T_0))/(C_2 + (T - T_0))$$

where η is the viscosity, T_0 is some reference temperature, and C_1 and C_2 are constants pertinent to the combination of the glass-forming material and reference temperature. If no specific knowledge is available of the material under investigation a combination of a reference temperature of T_g and the so-called universal values of C_1 (17.44K) and C_2 (51.6 K) can be employed.

Although, accurate numerical prediction within gastronomy is not relevant in most cases, the WLF equation gives an impression of the changes of the material properties as food materials are cooled during gastronomic processing. A set of constants, close to the so-called universal values, predict that the viscosity will change by 10 orders of magnitude over a temperature interval of about 20 °C.

Table 8 shows that the (calorimetrically measured) glass transition temperature depends strongly on the nature of the food components. For sugars the calorimetric glass transition ranges between -29 °C for xylitol and 110 °C for trehalose. The glass transition temperature of dry starch and dry starch components is high from the viewpoint of cookery (> 200 °C). The glass transition temperature of water has been heavily debated²³² and reported in a temperature range which can be considered irrelevant from the viewpoint of gastronomy. The diversity of glass transition temperatures gives the creative chef possibilities of manipulating textures of foods by interchanging components and changing the composition of ingredients.

Unlike the pure food components of Table 8, food is usually made out of mixtures. The glass transition temperature of such mixtures can be calculated as a weighted average of the glass transition temperatures of the individual

Table 9. Boiling Temperatures, T_b , Water Content W , Glass Transition Temperature, T_g , and viscosity, η , of Various Stages of Syrups^a

stage	$T_b/^\circ\text{C}$	W (% w/w)	$T_g/^\circ\text{C}$	$\eta(25\text{ }^\circ\text{C})/\text{Pa s}$
thread	110–111	20	-50	10^1
soft ball	112–115	15	-30	10^2
firm ball	118–120	13	-25	10^3
hard ball	121–130	8	0	10^6
soft crack	132–143	5	20	10^{10}
hard crack	146–154	1	50	10^{19}

^a Although not quantitatively accurately, these data give an impression of the ranges of material properties embraced by mixtures of the two components, sugar and water. Water contents were estimated from McGee,²³³ Chapter 12. Glass transition temperatures were estimated using the Gordon–Taylor equation from glass transition temperatures of water and dry sucrose. The viscosity was estimated using the WLF equation and the set of universal constants.

components. Various expressions have been reported for the calculation of the glass transition temperature of mixtures.²³¹ Most importantly, components with low glass transition temperatures strongly depress the glass transition temperature of mixtures; the effect is known as plasticization. The ever present solvent water is the most prominent and efficient plasticizer in food systems. The uptake of moisture is responsible for the loss of crispiness in many foods, for example, crackers, which can be treated as starch-based composites with glassy regions.

In the kitchen many sweet dishes involve boiling sugar syrup to various “stages”. Essentially, as water is driven off, so the solution concentration increases with a corresponding increase in boiling point (and decrease in the plasticization). The progress of the process is usually monitored by measurement of the boiling temperature and terminated at a specific temperature to obtain the required consistency (or “stage”). Of course, the glass transition temperature and viscosity of both the hot melt/solution and the cooled product all depend on the water content. The various stages of syrups are usually called thread, soft ball, firm ball, hard ball, soft crack, and hard crack. The glass transition temperatures and viscosities of the various stages is given in Table 9.

4.3.5. Gels and Gelation

4.3.5.1. Introduction to Gels. The original jellies are the aspics, meat-based jellies that arise naturally from the juices of boiled meats and bones. They get their name from the Latin *gelare* (to freeze), presumably as the hot clarified meat juices eventually set in a transparent solid on cooling. Thus, when the underlying structure was found to be that a solution of long molecules formed a three-dimensional network on cooling it is not surprising that the molecules identified as being responsible for the formation of the jelly were named gelatin.

Today we understand a gel to be a system where a large volume of liquid is stabilized in a solid-like form by a network of partially dissolved long-chain polymer molecules. Provided these long molecules form a complete three-dimensional network throughout the system it will have a solid-like behavior and becomes a gel. The properties of the gel then depend largely on the properties of this polymeric network. Since this network is normally very dilute and made up from molecules that are, more or less, random (although swollen by the presence of the surrounding liquid) it is reasonable in many cases to treat the network as a rubber-like system.

Most gels start off as a solution of polymeric molecules in a fluid (in food gels nearly always water, although alcohol- and oil-based gels are also possible). Some process whereby the molecules become cross-linked occurs; this may be chemical or physical. As more and more cross-links are formed, so the effective molecular weight of the dissolved polymer molecules increases and the viscosity increases correspondingly. As molecules form links to one another it soon becomes possible to build a full three-dimensional network throughout the solution, at which point it forms a gel. The cross-link density at which this full 3-D network occurs is sometimes referred to as the percolation limit.²³⁴

In a rubber the stiffness and extensibility are determined by the molecular weight between the cross-links and the equivalent segment length of the polymers. The simplest theories assume the molecules between the cross-links adopt random configurations with an equivalent segment length (l) being the length of a segment of a hypothetical molecule of the same total length (L) as the real molecule, which would ensure its end to end distance (r) is that predicted by that of a simple random walk. The stiffness, G , of the rubber is then given by $G \approx (3kT)/(2Ll)$ and the maximum extensibility λ_{\max} by $\lambda_{\max} = n^{1/2}$, where n is the number of segments in the molecule. Thus, a gel made from a more rigid molecule will have a longer equivalent segment length and, thus, for the same cross-link density will be correspondingly stiffer and less extensible. Similarly, for the same system if the cross-link density is lower the gel will be softer and more extensible. A further complication is that not all cross-links are stable. In some gels they are labile, so that the gel may flow to some extent and if broken has the chance to reform.

4.3.5.2. Methods of Gelation. There is a very wide range of possible gelation mechanisms depending on the type of junctions or cross-links and their relative stability. We can divide the junctions into two broad categories: chemical and physical. Chemical junctions are irreversible, while physical junctions can usually be undone as easily as they are made.

Examples of gels with chemical junctions in food are well illustrated in the cooking of eggs. Both the egg white and the yolks can form gels as they are heated. In both cases the covalent cross-links are created between the proteins once they have denatured. Both the denaturation and the cross-linking are thermally activated processes with different activation temperatures for different proteins. Egg whites will form a gel due to the denaturation and cross-linking of the albumin proteins at temperatures above ca. 52 °C, while the proteins in the egg yolks require a higher temperature (> ca. 58 °C). Conveniently, this provides a method of preparing perfect soft boiled eggs: simply place the eggs in a temperature-controlled water bath for a long time, enough for them to reach thermal equilibrium (~30 min) at a temperature above that at which the albumin will cross-link but below that at which the yolk proteins do so.

However, most of the gels we encounter in the kitchen are physical rather than chemical in nature. The most common is probably the gelatin gel. Despite the common nature of gelatin gels the details of the mechanisms by which the individual gelatin molecules become associated is still at best poorly understood.^{235,236} It seems that most if not all junctions involve several molecules and may be semiordered. It is probable that there are actually a range of different types of junctions, simple molecular entanglements, regions where pairs of molecules interact via perhaps mutual intertwining, and zones where several molecules come together to form

semiordered structures. Further, not all gelatins are equal; they come from different sources and have widely differing molecular weights, so the range of possible junction types may differ significantly between products. Overall, this leaves a complex situation for the chef. The minimum concentration of gelatin required to make a system gel depends on the ability to form a three-dimensional cross-linked network; so, shorter (lower molecular weight) molecules need higher concentrations. Thus, the gelatin gels can form and melt over quite large temperature ranges. For example, the concentration of gelatin appears to affect the melting temperature, more concentrated gels tending to have higher melting ranges. However, other properties of the solution (e.g., pH) can also affect the propensity for junctions to form as can the temperature. Some junctions only form at comparatively low temperatures, and others form very slowly, so a gel can change its properties on storage, usually by increasing the cross-link density, hence both making the gel stiffer and less extensible, in food terms providing a harder tougher gel. The only hard and fast rules are that the more gelatin used the stiffer the resulting gel will be.

Other gel-forming food molecules use a range of mechanisms to create the junctions. These include simple entanglements, electrostatic forces, e.g., the use of counterions to bind specific sites (alginates), local precipitation caused by pH changes, and crystallization.^{237–248}

In recent years a wide variety of gelling agents have found new uses in gastronomic restaurants. Here we give just a couple of examples. First, work at El Bulli by Ferran Adria using the fact that alginates can be made to gel simple by changing the counterion environment led to the process that has become known in gastronomic circles as spherification.²⁰⁰ The process can be used to make, for example, small spheres with a tough outer skin and a liquid center that look like and have a texture similar to caviar photographs of some examples, and the process can be found in *A day at El Bulli*,²⁴⁹ but which have any chosen flavor. An alginate solution with the desired flavor is prepared and then dropped into a water bath with a suitable solution of a calcium salt, as the solution falls so it forms into small spheres, as these fall into the calcium solution the outer layer gels quickly to create the “caviar”. One example of the use of this technique in the restaurant is the spherical green “olives” served on a spoon at El Bulli.²⁰¹

Another application of the properties of gelling agents is to exploit the fact that they can be quite temperature resistant; unlike gelatin gels which typically melt around 30–40 °C, some gels such as agar can have a melting temperature up to almost 100 °C. Such gels have been used as flavored layers in hot dishes to keep different foods apart. However, perhaps the most spectacular use is the flaming sorbet invented at the Fat Duck.⁶² Here a sorbet is doped with a suitable gelling agent (pectin) so that it will keep its shape even as the ice melts. Such a sorbet can then be flambéed at the table, providing a sorbet that is truly hot on the outside and completely frozen in the middle.

4.3.5.3. Gel Properties. Gels may be characterized by their main properties, e.g., hard, elastic, brittle, fluid, etc. Most of these properties are inherent to a particular system; within a particular system the degree of cross-linking can sometimes be controlled (up to a limit), and the concentration of the gelling agent can be varied. These two variables usually provide control over the stiffness of the gel but not over

Table 10. Some gelling Agents Used in the Preparation of Foods^{250–252}

gelling agent	conditions for gelation
alginates	sets in the presence of divalent counterions
agar	sets on cooling; thermoreversible mechanism involves formation of double helices
carageenan	gels when mixed with proteins
locust bean gum	gels on addition of various counterions including borates
gum arabic	gels at high concentrations and in acidic environments by partial precipitation of entangled molecules
xanthan	provides shear thinning gels; thermoreversible gelation
gellan	thermoreversible double-helix formation
pectin	gels at low pH and with divalent ions
cellulose derivatives	various derivatives form gels by swelling, or even wicking
gelatin	thermoreversible gels form on cooling

whether it is “brittle” or “elastic”; such properties are determined by the rigidity of the gelling agents themselves.

There is a wealth of gelling agents now available to the cook. Thus, it is possible to make gels that retain strength even when very hot (using, for example, agar as a gelling agent) as well as gels that form “crusts” on small liquid drops (using, for example, alginates that gel under changes in counterion content). The possibilities are almost endless. A list of readily available gelling agents that are approved for food use is provided in Table 10 together with some notes on the type of gels they produce and the conditions under which they form gels.

It is unfortunate that the precise conditions under which any gelling agent will form a gel always depends on the molecular weight of the specific material, but manufacturers rarely supply this vital information, so that the chef is usually reduced to carrying out some trial and error experiments to establish the best conditions for each specific application.

A particularly interesting class of gels are those formed by starches; these not only can be made in the kitchen but more often occur inside foods while they are being cooked. In the following section we will look at the structure of starch granules and how they form small gel particles when they are swollen and heated.

4.3.5.4. Swelling Starch, Including Potato, Rice, and Flour Cookery. Starch is formed by many plants in small granules; a typical granule may be a few micrometers across. Within a granule the plant lays down successive rings, each with a higher or lower proportion of amylopectin.²²⁴ In rings with a lower amylopectin content the molecules are packed close together in a well-ordered form, making these parts of the granules more resistant to attack from enzymes; such layers are often referred to as “crystalline”. The granules are not purely amylopectin and amylose; the plants also incorporate some proteins as they make the granules. Importantly, different plants (and different varieties of the same plant) incorporate widely differing amounts of protein in their starch granules.

The amount of protein and where it is located in the starch granules is crucial when cooking with starchy foods. Cold water added to starch granules will be absorbed by the proteins but hardly penetrate the amylose and amylopectin. Accordingly, high-protein granules absorb significant amounts of moisture at room temperature compared to low-protein starches.

Water absorption can be important as it affects greatly how the starch granules are used. If there are sufficient proteins

around the outside of a starch granule and they absorb enough water they can bind granules together. Once a large group of granules become bound, those near the center are unlikely to be further swollen by any additional water; this can be the origin of “lump” in sauces, etc.

While cold water will not greatly affect the amylose or amylopectin in a starch granule, hot water certainly will. When starch granules are heated the ordered “crystalline” layers start to melt as the temperature exceeds 60 °C. The actual melting temperature depends on the relative amounts of amylopectin and amylose and on how well the amylose molecules pack together to form small crystals inside the granules. This disordering and opening up of the structure of the granules allows water to penetrate. The linear amylose molecules are quite soluble in the water and the branched amylopectin less easily dissolved. As the molecules overlap with one another to a significant degree they do not fully dissolve in the water but rather form a soft gel. Starch granules can absorb an enormous amount of water without losing their integrity; this is one of the reasons why they are such good thickening agents. For example, potato starch granules can swell up to 100 times their original volume. This swelling provides the thickening effect of starches used in the kitchen.

The thickening of a sauce by ingredients such as flour or corn starch is an example of the gelatinization of starch granules into an optimal swollen state. Overcooking the sauce can result in a complete disintegration of granules, thereby releasing amylopectin and amylose into solution with the consequence of an undesired thinning of the sauce. Cooling a suspension of gelatinized starch results in gels where crystalline regions serve to link the amylopectin and amylose into an overall nonliquid structure. Further storage of such a gel can lead to the, usually undesired, so-called retrogradation, which is caused by recrystallization of amylopectin into a thermodynamically more stable form. The gel expels water and becomes denser and more heat stable during this process.

The baking of breads involves gelatinization of starch granules; during the cooling and initial storage of the fresh bread the amylose partly crystallizes and transforms the doughy texture of the crumb of very fresh or still warm bread into the more desired texture of a fresh bread. Further storage will lead to crystallization of amylopectin and formation of stale bread, which has a dry and hard sensation despite the fact that staling does not necessarily imply the loss of water.

Potatoes provide an excellent system to see what can be done with a starch gelling system. One can simply cook the potatoes and then mash them (mechanically break the major structures) so as to allow the starch molecules to absorb whatever liquid is present; typically potatoes can easily hold more than three times their own weight of additional liquid while still remaining firm enough to be eaten with a fork. Thus, it is possible to create a wide range of flavored potato dishes; traditionally fats such as butter or milk are often added to provide a creamy texture and flavorants such as garlic to provide a suitable savory note. However, in practice it is possible to use more or less any liquid to make mashed potatoes, so the water from red cabbages provides a distinctly flavored pink mash or the use of a dark beer provides a slightly bitter and malty tasting brown mash.

However, if the water content is low enough then, as we have seen previously, the starchy component can become glassy; then we have a crisp texture, as in chips (crisps in the United Kingdom). A further refinement is to create a

glassy texture on the outside, leaving a smooth creamy gel in the interior. This can be done in heavily processed dishes such as croquette potatoes, where mashed potato is rolled into suitable shapes and then fried to remove water from the outer layer, or in pieces of potato where no additional liquid has been added, such as French fries (chips in the United Kingdom). The key to crisp fries is to prevent water from the interior gelled starch migrating to the outer glassy layer and so reducing its glass transition temperature, rendering it soggy. A remarkable solution, pioneered at the Fat Duck, is to begin by cooking the fries in water until they are just about to break up; they will have absorbed some water during this stage and will form firm gels on cooling. Next, the cooled fries are dried by placing them in a vacuum desiccator; during this stage the outer layers become quite dry to the touch but of course still retain significant amounts of water. These fries are then put in oil at a temperature of around 110 °C to boil off the water in the outer layers and turn them glassy. Then, in a third stage the fries are put into hotter oil at ca. 190 °C; in this stage the glassy outer layer is temporarily softened and as steam is generated from the gel within it pushes much of the outer now softened glassy layer away from the interior, leaving a distinct puffed up nature to the fries. On subsequent cooling and serving the small air gap between the interior and exterior slows down diffusion of water, ensuring the crisp texture remains for at least as long as it takes the diner to eat the fries.

A similar interesting phenomenon is the popping of cereal grains; we are all familiar with popcorn. On heating, the outer layer of the corn, which is initially glassy in nature, softens to become rubbery. At the same time, pressure builds up inside the grains as some water in the slightly swollen starch turns to steam. If the balance is right, then there is sufficient pressure inside the grains to make them explode just as the glassy outer layer is soft enough that it can no longer withstand the pressure. The key to the process is to ensure there is enough water in the interior of the grains to generate the pressure and little enough water in the outer layers that they remain glassy until the temperature is high enough to convert enough water to steam to allow the grains to “pop”. More or less any grains can be popped if they are initially cooked in water to increase the water content at the center and then dried in a cool oven (at around 50 °C) to reduce the water content of the outer layers while leaving the interior well hydrated.

4.3.6. Cooking of Meat

4.3.6.1. Denaturation of Protein and the Associated Textural Changes. At the start of cooking meat has a flaccid feel. During the cooking process the most obvious changes are the shrinkage in muscle volume with a consequent loss of fluid and development of a rigidity absent in raw meat. The texture changes in the meat are related to all stages in the denaturation of the fiber and connective tissue proteins. The myosin begins to coagulate at about 50 °C, which gives the meat some firmness. The myosin squeezes out some of the water molecules which are further squeezed out of the cell by the sheath of connective tissue. In steaks and chops the water also escapes out of the cut ends of the fibers. At this stage meat is firm and juicy. At around 60 °C more of the proteins inside the cell coagulate and the cells become more segregated into a solid core of coagulated protein and a surrounding liquid. In this temperature range the meat progressively gets firmer and more juicy. At 60–65 °C the

denaturation of the collagen in the connective tissue happens. The collagen shrinks and forces the liquid out of the cells. At this stage the meat releases lots of juice, shrinks, and becomes more chewy and dry. A continued cooking leads to dryer and continuously more compact meat. However, at around 70 °C the connective tissue collagen begins to dissolve into gelatin and the muscle fibers are more easily pushed apart. At this stage the meat seems more tender, although the fibers are still stiff and dry because the fibers do not any longer form a substantial mass and because the gelatin provides a juiciness on its own.²⁵³

4.3.6.2. Meat Tenderness and Appropriate Cooking Methods. The ideal cooking of meat would minimize moisture loss and toughening of the fibers while also maximizing the conversion of collagen to gelatin. In ordinary kitchen practice this is difficult, and hence, the cooking method is usually adjusted to the meat's tenderness.²⁵³ The main difference between tender and less tender cuts of beef is the relative quantity of connective tissue. Tender meat has a small and the less tender a large proportion of the connective tissue. When cooking meat with a high content of connective tissue the point is to bring about hydrolysis of collagen and leave the fibers free to fall apart, in which case the meat appears to be tender. This can be accomplished by cooking the meat in the presence of water. If a little acid is added, the hydrolytic process is accelerated. Steam is even more efficient than water, and if it is under pressure so that the temperature is above that of boiling, hydrolysis is brought about rapidly. The methods using water or steam include braising and stewing. The dry-heat methods of broiling and roasting are used for the tender cuts since these presumably have so little connective tissue that none of it needs to be removed to make the meat tender.²⁵⁴

Cooking of tender meat can be a challenge since the desired temperature range is very narrow and it is difficult to obtain a uniform temperature in a piece of meat. When frying or grilling meat at a high temperature, a temperature gradient from the outside to the center will be present, which means the meat will dry out on the outside before reaching the desired temperature at the center. By using a long cooking time at a lower temperature this problem can be eliminated; however, a high temperature is needed for the desired browning reactions on the outside. This issue leads to the common kitchen procedure of heating the meat at a high temperature for a short time to obtain the browning (Maillard) reactions and finish the cooking at a lower temperature. The cook can also remove the meat from the heat before it is fully cooked and rely on the afterheat to finish the cooking more gradually. The ideal cooking time is affected by a number of factors such as the meat's starting temperature, the cooking temperature, flipping of the meat, fat content of the meat, and the extent of bones in the meat. Hence, there is no way of making a precise prediction of the ideal cooking time.²⁵³

4.3.6.3. Effect of Cooking Conditions on the Texture of Meat. In order to determine the optimum conditions for cooking of meat scientifically it is necessary to understand the heat-induced processes like the denaturation of the various proteins and the textural consequences, as described above. Several studies have investigated the effect of time and temperature on meat tenderness and the textural changes.^{255–257} Differential scanning calorimetry (DSC) is being used to investigate the denaturation of proteins by measuring the energy input when heating up the meat sample.

Table 11. Texture Changes in Bovine Muscle during Cooking, Relative to Thermal Denaturation of the Three Major Muscle Proteins^a

	molecular process		
	myosin denaturation	collagen denaturation	actin denaturation
firmness	++	(-)	+++
fiber cohesivity		---	
bite-off force	+	---	+
residual bolus		--	+
juiciness	(-)	-	---
total chewing work	++	---	++
total texture impression		++	--
denaturation temperature	40–54 LMM 53–60 HMM ^b	56–62	66–73

^a Sensory score increases and decreases with increasing temperature are represented by + and -, respectively. Number of signs represent relative size of respective texture changes.²⁵⁷ ^b LMM, HMM, represent low and high molar mass myosin respectively.

The Warner Bratzler method, which measures the shear force when cutting meat, has often been used to determine the tenderness objectively. However, the results do not often correlate to a sensory evaluation.²⁵⁸ Nevertheless, the shear force is a common method for meat quality assessment.

4.3.6.3.1. Detailed Description of Processes during Heating. An increase in shear force with increasing temperature occurs in two distinct phases. The first occurs at 45–50 °C and has been associated with denaturation of myofibrillar proteins (actin and myosin). Denaturation of actinomyosin leads to a release of tension and fluid is forced out of the space between the endomysium and the denatured myofibrils, accounting for the observed loss of fluid at these temperatures. The higher temperature (65–70 °C) increase in shear force is attributed to shrinkage of the perimysial collagen. The fibers are denatured and may be seen to change from an opaque inelastic fiber with characteristic banding pattern to a swollen fiber with elastic properties. The extent of shrinkage and loss of fluid depends on the nature of the intermolecular cross-links, which stabilize the perimysial collagen fibers. For this reason the extent of shrinkage is greater in older animals. Heating for prolonged periods at temperatures above 70 °C eventually causes a reduction in shear value, probably due to cleavage of peptide bonds in the molecule. The residual strength of fibers binding the muscle together contributes to toughness of the meat, in addition to the tension generated by the thermal shrinkage of perimysial collagen. Overall, the mass of the meat depends on the amount of denatured myofibrillar protein, while the texture is mainly determined by the collagen fibers of the perimysium. Two effects are involved: compression of the muscle bundles during collagen shrinkage and binding of the muscle bundles due to the residual strength of the denatured collagen fibers. In each case the effects are determined by the nature and extent of collagen cross-linking.²⁵⁹

4.3.6.3.2. Texture Changes Due to Denaturation (Time and Temperature). Martens et al.²⁵⁷ investigated the texture changes for beef during cooking. Table 11 shows the results interpreted in terms of thermal denaturation of the three major proteins.

From Table 11 it can be seen that both myosin and actin denaturation results in increased firmness, bite-off force, and total chewing work (usually referred to as toughness). Actin denaturation also results in increased amounts of residual bolus and has a negative effect on juiciness and total texture impression (the meat becomes drier). Denaturation of collagen leads to reduced fiber cohesivity, bite-off force, residual bolus, juiciness, and total chewing work and increased total texture impression (in everyday terms, tenderness). This means that to achieve the optimal eating experience the meat

should be heated to a temperature where collagen is denatured but actin is still native, i.e., between 62 and 65 °C.²⁵⁷ The rate of actin denaturation is dependent on time as well as temperature; at 66 °C denaturation of 10% of the actin is accomplished in approximately 10 min, 50% denaturation in approximately 40 min, and 90% denaturation in approximately 100 min.²⁵⁷

Tornberg²⁶⁰ suggests that the denaturation of sarcoplasmic proteins has a big impact on the texture of the meat, as the denaturation below 50 °C causes increased toughness of the meat but in the temperature range 50–65 °C makes the meat appear more tender as these proteins form a gel in the space surrounding the fibers and fiber bundles. At temperatures above 65 °C this gel is much firmer and leads thus to a less tender texture.²⁶⁰ This is in accordance with the results found by Martens et al.²⁵⁷

4.3.6.3.3. Pressure. Ma and Ledward²⁶¹ studied the effect of pressure (0–800 MPa) on the texture of beef muscle. They found that a pressure of 200 MPa caused a large significant decrease in hardness, chewiness, and gumminess (evaluated by texture profile analysis: Stable Micro System Type) in the temperature range of 60–70 °C. By using DSC the texture changes were further analyzed. Collagen was, as expected, inert to pressure, whereas myosin was unfolded by both pressure and temperature. From the results obtained it was concluded that the structurally induced changes are unlikely to be a major cause of the significant loss of hardness observed when beef is treated at 60–70 °C and 200 MPa. Instead, accelerated proteolysis under these conditions is suggested.

4.3.6.3.4. Heat Transfer. The heat-induced processes, as described above, all depend on the heat transfer in a piece of meat when cooking. Some studies have worked on the modeling of heat transfer in meat. Most studies are mainly concerned with the safety issue (i.e., when does the meat reach 75 °C in the center^{262–266}), but a few studies have been conducted on the impact of heat transfer on the textural properties.^{267–270}

Modeling heat transfer in meat is an immensely difficult task. Meat is seldom uniform in size or shape; it consists of several fractions of protein each with their own thermal properties, and a large number of processes occur during heating. These processes will cause changes in the thermal properties, e.g., changes in heat capacity, thermal conductivity, etc., and changes in dimensions, water-holding capacity, etc. Furthermore, water is transported in the meat during heating, which leads to transport of heat and, if the temperature is high enough, evaporation of water at the surface. To complicate things further the fiber direction also plays a role in the heat transfer. However, understanding the basics of heat transfer in meat (and using a thermometer

when cooking) can lead to improved gastronomic quality of cooked meat, as this will reduce the risk of overcooking.^{271–273}

Califano et al. simulated the heat transfer during the cooking process of beef and the related textural changes. They propose a model for the cooking process as a tool for analyzing the effect of cooking operations on the texture of meat. The effect of heat transfer coefficient, temperature of the cooking medium, and size of the meat piece on the hardness (by the Warner Bratzler method) of the cooked meat was studied. If the cooking medium was above 85 °C the average hardness was high regardless of processing time. Conversely, a low temperature gives a more tender product.²⁶⁷

4.3.6.3.5. Marinating Meat: Softening. Marinating, immersing meat in a fluid medium, has been used for many years to flavor meat as well as tenderize it in the domestic kitchen. Marinating of meat can be considered as a chemical method to help tenderize meat, which also changes the flavor of the meat. The literature on this topic is however driven mostly by the demand in the food industry to tenderize meat. Marinade solutions can improve the perceived juiciness and tenderness of the meat as well as increase the weight of the product. However, there is a particular problem with marinating meat in that the marinade penetrates the meat very slowly and hence only works on the outer layers. This problem is sometimes overcome by injecting the marinade into the meat.

Several studies have investigated the properties of tenderizing agents, focusing on obtaining the optimal juiciness and tenderness without causing any undesirable effect on color or flavor. The mechanisms for increased tenderness and juiciness are generally connected with higher water holding capacity (WHC) and swelling of myofibrils.

Acids, like vinegar, lemon juice, or wine, are very common ingredients in a marinade. Sour marinating of meat has been found to improve tenderness and juiciness and increase the weight of the product due to retention of water. However, sour marinating is also found to affect the flavor, giving an unpleasant sour taste.^{274,275} The mechanism behind the tenderizing action of acidic marinades is shown to involve increased proteolysis and increased conversion of collagen to gelatin.²⁷⁶ The pH value is important to the swelling capacity and hence the WHC of meat. Both low and high muscle pH after marinating have positive effects on texture and give an increase in water binding capacity and swelling of myofibrillar protein.^{277,278} As the pH moves further from the isoelectric point, the water-holding capacity increases due to an increase in the amount of negative charges on the meat proteins that can bind water.^{279,280}

Since an increase in WHC on either side of the isoelectric point is seen on the myofibrillar protein, alkaline solutions also have tenderizing properties. Alkaline marination is a common method of tenderization in Chinese cookery,²⁸¹ and it is likewise commonly used as a marinade in household cooking in India.²⁸² A study by Hsieh et al. in 1980 showed that bicarbonate treatment caused swelling and fusion of the myofibrils and obscured the structures within the sarcomer. Although alkaline marinating generally has been overlooked in the West, recent work has focused on using bicarbonate to minimize the problem of pale, soft, and exudative (PSE) pork meat.

Wynveen²⁸³ found that postmortem injection of sodium bicarbonate and sodium phosphate improved WHC and color in pork. Likewise, Yang²⁸⁴ found that postmortem injection

of sodium bicarbonate in meat gave an increase in WHC and solubility of myofibrillar protein as well as decrease in drip loss, weight loss during cooking, and shear force. Sheard²⁸⁵ compared the effect of sodium bicarbonate with that of salt and phosphate, which are also common tenderization agents in the food industry. All solutions gave a significantly higher yield and a decrease in shear force. The effect of sodium bicarbonate on shear force and cooking loss was as great as salt and phosphate. However, the bicarbonate-treated samples contained air-filled pockets between fibers, giving an unusual appearance that might not be appreciated by consumers. This problem might be caused by generation of carbon dioxide produced during cooking, which is likely also to be a contributing factor for the texture change. A recent study by Anna et al.²⁸⁶ investigated the synergistic effect of sodium bicarbonate and blade tenderization on tenderness of buffalo rumen meat. They found that sodium bicarbonate gave improved tenderness based on analytical and sensory analysis.

The alkaline marinating techniques used in some places in Asia can be compared to the traditional Swedish/Norwegian way of preparing dried fish (lutefisk).¹⁶⁶ Drying was a common way of preserving fish (it can keep for years in Arctic climate), and preparation of lutefisk was a primitive way of reconstituting the moistureless tough fish. Lutefisk is made by soaking the dried cod in fresh water for a week, then submerging it in a alkaline solution for several more days, and resoaking it in fresh water for another 2 days.²⁸⁷ Originally the ashes from a wood fire (rich in carbonate and minerals) or lime stone (calcium carbonate) and later lye (sodium hydroxide) was used.¹⁶⁶ The fish becomes very soft after cooking, which can be explained by the fish proteins accumulating a positive charge in the alkaline solution. This causes the proteins to repel each other, and only weak bonds are formed between the muscle fibers, giving a soft texture.¹⁶⁶

Another chemical way of tenderizing meat is by using enzymes. For many years the Mexican Indians have known that the latex from the papaya leaves has a tenderizing effect on meat during cooking. The major enzyme, papain (a cysteinyl-proteinase), has been investigated. It has little effect at room temperature, so the main action occurs while cooking. Above 50 °C the collagen structure is loosened and vulnerable to attack from the proteinase,²⁸⁸ unless the enzyme is deactivated it will continue to attack the collagen until none is left and the meat has fallen apart. Ashie et al. in 2002²⁸⁹ compared the use of papain and an aspartic protease (expressed by *Aspergillus oryzae*) for their tenderizing effect on meat.²⁹⁰ They found that aspartic protease has an advantage over papain by having a limited specificity on meat proteins and being readily inactivated by cooking. Additionally, the use of proteases from kiwi fruit,²⁹¹ bromelain from pineapple, and ficin from figs²⁹² has been reported.

4.4. Cooking Methods and How They Work

Most cooking techniques have been around in one form or another for many centuries, but often they are not well understood by those who use them. In this section we try to describe the basic physics and chemistry in the traditional cooking techniques used in the kitchen so that chefs will be able to avoid such “schoolboy” errors. Then we shall move on to describe how “new” methods can be introduced by adapting the equipment found in the science laboratory. Indeed, this process has already started to have a real impact in some kitchens where, for example, the introduction of

laboratory-style temperature-controlled water baths permits much finer control of the cooking process and thus at the same time both improves consistency and reduces waste.

4.4.1. Traditional Cooking Methods

4.4.1.1. Use of Heat. Many cooking methods or gastro-nomic unit operations involve heating the food material to induce chemical and/or physical changes that favor the development of pleasant flavors and textures and create microbiologically safe food. However, we also often heat food simply so as to serve a hot meal. Gastronomic foods are often served above room temperature (for example, warm salads) even when there are no specific physical, chemical, or microbiological reasons for the heating. However, heating the food enhances the release of aroma compounds, changes the perception of the food, and can create the direct sensation of heat.

During heating the elevated temperatures will shift the thermodynamic stability of food components and make chemical changes and especially phase transitions possible (e.g., melting, evaporation, gelatinization, denaturation of proteins). Through such transitions the food itself can be transformed: plant cell walls can be broken, making vegetables soft, meat protein can be denatured, rendering it tougher, etc. For the gastronomic cook it is important to be aware of the range of possible transformations and their impact on the flavor and texture of the food being heated.

Elevated temperatures change the rates of chemical reactions; chemical compounds that are otherwise metastable may become unstable, and severe changes may take place within the time scale of the cooking process (minutes to days). For example, proteins may be hydrolyzed into peptides and amino acids during the cooking of stocks, Maillard reactions will take place during the frying process at elevated temperatures, etc.

The phase transitions that occur in foodstuffs are mostly strongly endothermic. The demand for significant amounts of heat can in turn influence the cooking process by perturbing the dynamics of transport of heat and moisture. Since most foods have rather high water content, the evaporation of water is a particularly important phenomenon for understanding most cooking methods.

Water has a particularly high specific heat (heat capacity), 4.19 kJ/K. Accordingly, the energy needed to heat 100 mL of water from room temperature to (normal) boiling point is about 31 kJ. However, a much more important issue is the high latent heat of evaporation of water (2.26 MJ/kg). Thus, the energy needed to evaporate 100 mL of water is about 222 kJ; about 7 times more heat is needed in order to evaporate water as compared to heating it from room temperature to boiling temperature. This large heat requirement is one of the more important limiting factors in the kitchen, especially when scaling up recipes.

The temperature distribution in food during preparation can be strongly influenced by evaporation phenomena. Since many food ingredients are very moist their thermal behavior can be modeled, to a first approximation, by the behavior of pure water. In cooking operations where the surface temperature can exceed 100 °C (e.g., frying) a dry crust has to be developed in order for the local temperature to be above that of boiling water; the loss of water enables high temperature and accompanying acceleration of chemical reactions such as the Maillard reactions specific to the frying process.

The presence and evaporation of water affect the transport of heat through foods as they are being cooked. In particular, they tend to reduce the rate at which the temperature at the center of foods being cooked increases and thus also increase temperature gradients within the food.

4.4.1.2. Heating Methods. *4.4.1.2.1. Boiling.* Boiling (heating in boiling water) is perhaps the simplest of all kitchen techniques. For most vegetables we can assume that the temperature is close to 100 °C (of course, addition of salt or changes in atmospheric pressure will affect the boiling temperature, but such changes are generally small). We can then treat the cooking process as a relatively straightforward heat transfer problem with the boundary conditions of a uniform constant temperature (100 °C) at the food surface. Thus, cooking times will be reproducible.

The time required to cook different foods will vary greatly; the actual temperature required will differ between foods. In many cases, food is cooked for a short time in boiling water, creating a significant temperature gradient across the food. Consider, for example, green beans cooked for 3 or 4 min. The surface temperature will be 100 °C, while the center will have a temperature of only around 30 °C. As the food is left on a plate heat continues to flow to reduce (and eventually remove) this temperature gradient.

In some foods we wish to ensure that some physical or chemical process proceeds. In such cases the time scale of the cooking process may be much longer than that of heat transport, leading to fewer temperature gradients within the food during the cooking process. Examples where longer cooking times are used include the need to gelatinize starch in cooking of rice (and to a lesser extent potatoes) and hydrolysis of proteins, which is required to provide the flavor of stocks.

Some complete dishes are prepared in boiling water. We can consider stews and some sauces simply as a dilute solution with solutes of low molecular weight (salts, amino acids, etc). The boiling takes place close to the normal boiling point of water (any boiling point elevation due to the dissolved salts is of no practical importance). The temperature will remain uniform as long as there is no accumulation of solid material at the bottom of the pan near the heat source, in which case it can start to overheat and “burn”; stirring is required to prevent this from happening.

In the kitchen there are many different ways to describe boiling water. The main differences are simply in the rate of heat input. The minimum heat input is that which will just maintain the temperature at 100 °C with the minimal amount of evaporation of steam. As the heat input is increased, so the rate of creation of steam and the rapidity of bubbles rising to the surface increases; at some heat input the flow caused by the bubbles becomes rather chaotic, leading to violent movement and mixing of food in the pan.

Gentle boiling with minimum heat input, just enough for ensuring the boiling of water, is usually termed “simmering”. Some chefs claim that simmering causes less toughening of meat than more “rapid” boiling, although to our knowledge there is no actual evidence for such an effect. However, it may be that the heat input in these cases is not sufficient to maintain the water at boiling point and the actual temperature was significantly lower, in which case a more tender product could be quite possible.

At the opposite extreme with a high heat input chefs often say water is at a “rolling boil”, indicating the large-scale movements in the water. If food is added to a pan at a “rolling

boil” the heat input may be sufficient to avoid a significant temperature drop as the cold food has to be heated, thus reducing the cooking time, and the violent movement of the water may ensure the food is kept moving and prevented from sticking to itself. However, there is no literature where any clear distinctions are drawn, and personal experience suggests these are not important effects.

4.4.1.2.2. Steaming. In the steaming process the food (such as vegetables, fish, or bread dough) is in contact with steam above boiling water. Heat is transferred to the food as the gaseous water condenses at the food surface and releases its latent heat. The steam is thus a very effective medium for transferring heat as opposed to hot air at the same temperature (as seen in the baking process). One could consider steaming as the opposite of baking, condensing rather than evaporating water at the food surface. No crust is formed, and the food is not dehydrated, which creates very different results. In steaming the surface temperature is 100 °C due to the equilibrium between the two states of water.

Steaming thus resembles boiling and simmering in many respects, although some differences may be important. The food is not immersed in water, so that probably fewer soluble compounds are lost from the food. Steaming is generally believed to create textures with a better bite and is a more gentle form of heating compared to boiling.

4.4.1.2.3. Frying and Deep Frying. In frying a much higher temperature is used than when cooking in water. In deep fat frying the oil temperature is usually around 160–180 °C. The surface temperature of food is thus well above the boiling point of water, and rapid boiling occurs. This boiling requires a large amount of heat, so the temperature of the cooking oil normally falls rapidly, leading to a reduction in this surface boiling. In practice, the amount of food put in a deep fat fryer will greatly affect the way in which it cooks. If too much food is put in at one time the temperature is reduced below 100 °C and the food will not become “crisp”.

Shallow (or dry) frying uses a high (surface) temperature (typically 200 to 240 °C) and, usually, some frying oil to ensure a good heat conduction. The surface temperature is (unlike boiling) controlled by a balance between the heat needed to evaporate water and the supplied heat from the stove. Unlike the boiling of water, there is no phase transition to control the temperature of frying oil or the pan surface. The temperature remains nonuniform throughout the frying process due to evaporation of water.

Two main transport processes take place: heat conduction from the hot surface toward the center and transport of water toward the surface where water is evaporated (of course, it can evaporate from any surface, but most evaporation will come from the hot surface in contact with the pan). A dry, hot, and relatively well-defined frying crust is built up. Just below the crust the temperature is expected to be close to 100 °C due to evaporation of water. Thus, a large temperature gradient is created over the frying crust. The temperature of the crust surface is comparable to the frying oil. If the temperature in the crust is high enough, browning reactions can take place at considerable rates.

The temperature at the center of the food item will however only slowly increase with time as heat is conducted inward. For example, in the case of steak frying, the process is terminated when the temperature has reached 40–60 °C, giving the center an appropriate red color. This can take (for a typical 3 cm thick steak) between 5 and 12 min.

During heating the food (especially meat) releases considerable amounts of water (due to changes of meat at temperatures above the denaturation temperature of muscle proteins). The energy input must match this release in order to quickly evaporate all the water so as to keep the surface temperature of the food well above 100 °C. Too little power will result in a cooking/broiling process where the surface temperature will be close to 100 °C, giving rise to less browning and a different flavor formation. It is often forgotten by cooks that they should not attempt to cook too many steaks (or brown too much meat) at a time. The amount that can be cooked is limited by the power of the burner used on their stove. The power of the burner must be significantly greater than that required to boil off the water that is being released from the cooking meat. This problem is particularly important when scaling up recipes. A recipe that works well when cooking for four may completely fail when doubled for a dinner party of eight all because the pan temperature cannot get above 100 °C with the increased amount of meat.

The heating power of the burners on modern domestic stoves is typically up to 2.5 kW, while restaurant stoves can often provide up to 8 kW. The power limits the amount of meat that can be browned at a time; for a domestic stove the limit is around 800 g, and for a commercial stove it is nearer 2.5 kg.

In a wok or when using any continuously stirred process the surfaces in contact with the pan will heat up briefly. The surfaces facing away from the pan will quickly be cooled down due to evaporation of water. The average surface temperature during stir frying is thus quite low (below 100 °C). Heat conduction into the vegetable is thus quite slow and gentle despite the high surface temperature of the wok. The center temperature of the end product will be low compared to a boiled vegetable; this will ensure less transformation of the cell wall carbohydrates, etc. However, the vegetables are subjected to severe dehydration. The combination of gentle heating and dehydration gives the product its texture or bite. In meats, the Maillard reactions and pyrolysis at the surface ensure development of taste and aroma compounds.

4.4.1.2.4. Baking. In a baking oven the air temperature is kept fixed in the range 150–250 °C by a thermostat system. Air circulates the oven due to convection or forced circulation. Confusingly, some manufacturers (particularly in the United States) refer to ovens where the air is circulated using a fan as “convection” ovens.

Oven surfaces and heating elements may have much higher temperatures so that some radiant heating can also occur.

(a) Leavening of Cakes, Breads, and Soufflés. The expansion of various baked goods during the heating can be created by several kinds of endothermic processes where the thermodynamic equilibrium is shifted by the increasing temperature. For example, in the endothermic decomposition of baking powder into gaseous compounds carbon dioxide is formed from sodium bicarbonate (baking soda) or carbon dioxide and ammonia are created from ammonium bicarbonate. Dissolved gases can be released and water can evaporate. At elevated temperatures the equilibrium of these processes will be shifted toward the formation of more gaseous compounds, so that the baked goods rise due to an increase in the gas content.

Industrially, but not so much in home cooking, leavening acids are used. These leavening acids (such as sodium

aluminum sulfate, dicalcium phosphate dihydrate, potassium acid tartrate, or δ -gluconolactone) enable the decomposition of bicarbonate at lower temperature and prevent the pH elevation and soapy flavors due to formation of carbonate ions. The action of leavening acids is kinetically determined and can be classified into slow, medium, and fast reacting.

(b) Role of Water Evaporation for the Expansion of Bread Cakes and Soufflés. The dough or soufflé base is very moist with water activity (relative humidity) close to 1. Therefore, in many respects they can be treated as if they behave like water. The doughs belong to the colloidal category of foams containing many small air bubbles. The air is trapped within a soft material and is thus approximately subjected to pressure very close to the external pressure, which usually is close to 1 atm. The entrapped dry air can be a result of mechanical treatment of the dough, leavening using yeast, or leavening using baking powders. In the case of soufflés since no yeast or baking powder is used, evaporation of water is particularly important and the main cause of the rising of the soufflé.

During the baking process the macroscopic transport of heat and moisture over distances comparable to the cake/bread/soufflé size are rate limiting and responsible for the overall duration of the baking process. On a much shorter time scale we can expect water to evaporate into the air bubbles of the dough in order to attain a local equilibrium between gaseous and liquid water. Some water will be lost from the surface of the soufflé, but the inside will remain a very moist structure. It is reasonable to assume the pressure of water will attain its equilibrium-saturated value inside the bubbles.

At elevated temperature the saturated water pressure will increase and ultimately approach the external pressure (1 atm at 100 °C). Likewise, the molar and volume fraction of water in the gas phase increase (ultimately to 1). Due to the dilution effect of the gaseous components already present (N_2 , O_2 , Ar, etc.) a large amount of water has to evaporate, making the overall gas phase expand. Under these somewhat simplified assumptions the gas volume will in principle diverge when the equilibrium partial pressure of water approaches the external pressure (at the boiling point temperature of water)

$$V_{g,\text{total}}(T) = V_g(T_0) \frac{T}{T_0(1 - p_w^o(T)/p_{\text{ex}})}$$

where $V_g(T_0)$ is the volume of dry gases at low temperature (T_0), $p_w^o(T)$ is the temperature-dependent saturated vapour pressure of water, p_{ex} is the external pressure, and T is the absolute temperature.

The total gas volume is proportional to the initial volume of dry gases. The expansion mechanism due to water will only work if other gaseous components are present. In other words, evaporation of water will boost other leavening mechanisms. In a soufflé, the chef beats in air in the egg white before cooking; during baking this increased air volume is further boosted by evaporation of water. The normalized gas volume as a function of temperature for an idealized model air/water soufflé is shown in Figure 17. The trivial temperature expansion of the dry air contributes in itself with an almost negligible expansion, whereas evaporation of water contributes dramatically when approaching the boiling temperature.

All the various mechanisms of heat-assisted rising of bakery products, do not work independently but mutually

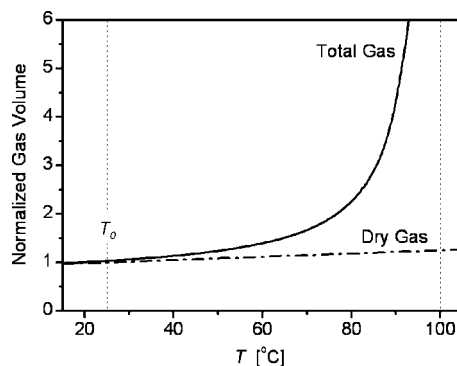


Figure 17. Expansion due to evaporation of water shown as normalized gas volume as a function temperature. The volume is normalized with respect to the volume of dry air at $T = 25$ °C. The external pressure is taken to be 1 atm, and the volumes are calculated using data for saturated vapor pressures of water from the *Handbook of Chemistry and Physics*, 79th edition. The initial volume of dry air shows an expansion which is proportional to the absolute temperature, whereas the volume taken up by the gaseous water will diverge when the temperature approaches the boiling point of water. The expansion of a soufflé is of the order of about 3 times corresponding to an (average) temperature of close to 90 °C, which is somewhat higher the typical center temperature for white breads (close to 70 °C).

boost one another other. For example, the expansion due to evaporation of water will influence the equilibrium between dissolved and chemically bound carbon dioxide and gaseous carbon dioxide. The expansion due to evaporation lowers the partial pressure of carbon dioxide and thus favors release of more gaseous carbon dioxide in order to restore equilibrium. At the same time, the released carbon dioxide boosts the expansion due to evaporation of water.

4.4.2. “New” Cooking Techniques

4.4.2.1. Microwaves. It is the dipolar nature of water molecules that permits them to be heated by microwaves. The alternating field (typically 2.45 GHz in a domestic microwave oven) causes the dipoles to rotate; the inability of the dipoles to keep up with the field leads to the heating effect. Any dipolar material will be heated in a microwave oven, but water having the strongest dipoles in common food stuffs displays the greatest heating effect. In general, any material with hydroxyl groups will display dipolar heating in a microwave field; thus, oils, sugars, proteins, and carbohydrates can all be heated to a greater or lesser extent with a microwave oven. However, materials where the dipoles are not able to rotate (such as ice) are much less susceptible to microwave heating.

It is worth realizing that the microwave energy will always be absorbed from the outside inward (in general, the higher the dielectric constant the greater the absorption). In wet foods the typical penetration depth of microwaves is a few centimeters. The common myth that microwaves heat from the inside out probably arises from reheating foods such as jam doughnuts where the outer regions have significantly lower water content than the center so that the center can become hotter than the outside.

An interesting example of the use of a microwave oven to produce a novel food was described by Nicholas Kurti in his highly influential 1969 Royal Institution lecture⁹ which perhaps can be traced as the origin of the modern science of Molecular Gastronomy. In the lecture he demonstrated the concept of an “inside out” Baked Alaska, by freezing ice

cream at low temperatures, leaving very little liquid water, and placing some very high sugar content jam which retains a significant liquid content at the center; he was able to use a microwave oven so that the microwaves were hardly absorbed by the ice and passed through heating the jam center, thus producing a novel dessert with a cold outside and a hot center.

However, despite this early potential novel use of a microwave the device has not found many real gastronomic applications, perhaps due to the nonuniformity of the heating (there are always nodes and antinodes separated by a few centimeters in a microwave oven) or maybe to the fact that it is very difficult to achieve temperatures above 100 °C so that browning and Maillard reactions do not usually occur. Of course, a variety of methods have been introduced to permit browning in microwave ovens: the use of containers that themselves heat up or the use of combination ovens which have conventional as well as microwave heating.

It is instructive to note that boiling water in a microwave oven is (in certain cases) very different than boiling water in a kettle. In a conventional kettle the element (or for a kettle on a stove the base) is heated to a temperature well above 100 °C and the water starts to boil readily at this hot surface. However, in a microwave oven the water is heated directly, so that it can superheat if no bubbles are nucleated. In practice, tap water has a good deal of dissolved air which starts to come out of solution as the water is heated (the solubility of the gas being lower at elevated temperatures), and this leads to the nucleation of bubbles and allows the water to start to boil as soon as the temperature reaches 100 °C. However, in previously boiled water in which there is no dissolved air, it is quite possible for the water to superheat significantly. If this happens and you remove say a cup of reheated coffee from the microwave oven that has superheated and not yet started to boil it can at the least disturbance (for example, adding a little sugar) boil over in an explosive fashion.

4.4.2.2. High Pressure. Some useful processes in cooking, such as extruding, pressure cooking, and homogenization, use moderately elevated pressures. In these cases it is the increase in the boiling temperature of water with pressure that provides the useful effects. In this section we are concerned with the effects of cooking at much higher pressures where more interesting effects can be found.

The use of high-pressure techniques in the pressure range from 2000 to 10 000 atm, where pressure effects become significant, has been limited for technical reasons; the exploration of the technique is not new. Hite²¹⁶ used pressure as a means of microbial control in milk as early as 1899. Pressure treatment normally has no effect on covalent bonds but denatures proteins, as denatured proteins have smaller partial molar volume than native proteins owing to differences in solvation. High-pressure processed foods commercially available today included juices with noncooked flavor but with long shelf life, dried cured hams, where residual microbial contamination following slicing has been removed without heat treatment, and products such as guacamole where browning enzymes are deactivated by pressure. Equipment for high-pressure processing is becoming less costly and will eventually find its way to the restaurant kitchen, opening up possibilities for new types of dishes. Meats can be decontaminated by pressure treatment prior to shorter heat treatment such as in a wok or heat treatment at lower temperatures. Eggs can be hardened by

pressure treatment instead of boiling but with preservation of the fresh egg flavor. Milk can be solidified by pressure without requiring acidification and addition of sugars, creating new pH-neutral types of deserts. The effects of pressure on fat crystallization deserve further attention for optimization of spreadability and smoothness. The drawbacks seem few except for the cost of equipment. One potential drawback is that lipids in poultry show increasing oxidation following pressure treatment and subsequent cooking.²⁹³ It should, however, be possible to define pressure–temperature–time windows, where microbial decontamination is acceptable without pressure-induced lipid oxidation.

Pressure effects on ice are unique as pressure lowers the melting point of normal ice down to almost –20 °C around 2000 atm. Pressure-assisted freezing involves pressurizing up to 2000 atm followed by cooling to below zero. Upon pressure release, water in the subzero liquid food item solidifies all at once, not just from the outside, to form smaller ice crystals than normal methods. Pressure-assisted thawing, which has already been used to prepare of raw fish dishes from frozen fish without lengthy thawing at room temperature or thawing at high temperature, depends on an initial pressurization of the frozen fish during which the ice melts at the low temperature followed by a controlled pressure release with simultaneous temperature compensation to reach ambient pressure and temperature. The technique produces a fish which is thawed uniformly and without high-temperature domains.²⁹⁴

High-pressure techniques should find their way to the kitchen for creation of new dishes, where freshness and uncooked flavor can be combined with changed texture.

4.4.2.3. Improved Temperature Control. One area where commercial kitchens have already learned from the science laboratory is in the use of accurately controlled temperature baths. Until quite recently a kitchen “bain marie” was simply a warm water bath; the temperature might have been anything from 40 to 80 °C. Temperature control (if any) was via a crude bimetallic strip type of thermostat, and temperatures were set using a simple variable resistor, usually with no calibration at all. However, in the past decade or so many restaurant kitchens have started using recirculating water baths with modern, accurate temperature controllers (the same as those found in any good laboratory). The results are immediately noticeable. Precise temperature control permits all sorts of cooking that is not otherwise possible. For example, an egg can be cooked in water at 52 °C, a temperature where the white will set but the yolk will remain fluid; thus, perfect poached or soft-boiled eggs can be served to order with complete confidence that the product on the plate will be quite perfect.

Another use for such baths is in *sous vide* cooking of meats. Meat is placed in a plastic bag and sealed under vacuum to exclude any air and provide a barrier between it and the surrounding water (or other heat transfer medium). Of course, care is taken to ensure any bacteria are killed prior to the low-temperature cooking, either by quick pasteurization in a hot (85 °C) bath for a couple of minutes or by passing the flame of a blow torch over the surface of the meat before putting it in the bag. The meat is then cooked at a low temperature, where the myosin and actin proteins are scarcely denatured, but for a sufficiently long time that the collagen is slowly softened. The required temperatures and times vary according to both type and cut of meat. Thus, for example, a lamb fillet might require 90 min at 56 °C,

while belly pork might take 6 h at 60 °C. The best results are found by trial and error, but chefs who use the technique find significant differences in the texture and flavor of meats cooked at temperatures that differ by as little as 1°C.

4.4.2.4. Low Temperatures. Another area where modern laboratory equipment can be of real use in the kitchen is in cooling. Freezers used in the kitchen typically can only reach temperatures down to -20 °C. However, many processes demand lower temperatures. For example, to kill some parasites, etc., in some fish it is necessary to cool them below -30 °C. Similar low temperatures are needed to prepare ices with high alcohol content and foods for freeze drying. In this context, freeze dryers are also potentially useful kitchen appliances (and are already in use at some restaurants).

Liquid nitrogen can be particularly useful in the kitchen; it not only provides quick and easy access to low temperatures but also permits rapid cooling of all sorts of foods and so prevents the growth of large ice crystals that so often damage frozen foods. Two particular uses for liquid nitrogen are to permit the easy grinding of herbs; simply mixing the herbs with some liquid nitrogen in a mortar quickly freezes them into brittle solids, and grinding with the pestle turns these into a useful powder that can be used to provide an instant hit of fresh flavor in any dish. However, perhaps the best use of liquid nitrogen was pioneered in 1901 soon after nitrogen was first liquefied by Wroblewski and Olszewski in Warsaw in 1887²⁹⁵ by Mrs. Agnes Marshall.^{296,297} Mrs. Marshall was the celebrity chef of her day, giving large-scale demonstrations and selling her recipes, books, and equipment along the way. Unfortunately for us on her death all the rights to her work were bought up by Mrs. Beeton's publishers and never again saw the light of day. However, she describes in some detail how to use liquid gases at the table to prepare ice cream. The principle is extremely simple: you just add liquid nitrogen to the ice cream mixture and stir while it freezes; it is possible to freeze a liter of ice cream in under 20 s in this way.^{298,299} The advantage is that the speed is so great and the temperature so low that only very small ice crystals can form, making a wonderfully smooth ice cream.³⁰⁰

4.4.2.5. High-Power Mixing and Cutting Machines. A further group of items of modern equipment that is finding increased use in the kitchen are powerful mixing, grinding, and cutting tools. One of the most interesting of these is one that was indeed designed for the kitchen, the Paco Jet. The Paco Jet consists of a very sharp knife that rotates at around 2000 rpm and is driven slowly into a solid frozen block of food, shaving layers of thickness (ca. 1 μm) in each revolution.³⁰¹ The machine is most commonly used to produce ice creams and sorbets. It can produce particularly smooth ices by ensuring the crystals are kept very small. To ensure all the ice crystals are cut into pieces that are small enough that we can hardly detect them it is important that the block is completely solid (i.e., frozen to a temperature below the eutectic point for the solutes, sugars and proteins, present), which for most ices would mean a temperature below about -18 °C. The machine has a suitable headspace above the solid block to permit aeration of the resulting mixture, while it is still fully frozen so as to produce light ices.

Another useful high-power technique can be to use ultrasonic agitation to induce emulsification. A simple ultrasonic probe placed in a small container of oils and aqueous liquids will very quickly emulsify the mixture;

provided suitable emulsifiers are present, the resulting emulsions can be very stable. This is a particularly easy way to prepare small emulsions; typical probes have diameters of 1 cm or less, so volumes of 1 or 2 mL can be prepared to order.

5. Enjoyment and Pleasure of Eating: Sensory Perception of Flavor, Texture, Deliciousness, Etc

In this section we start to deviate from chemistry and move into psychology and sensory science. In particular, we want to begin to understand what factors influence our perception of "pleasure" and our enjoyment of the meal.

5.1. Flavor Release

The chemistry of the formation and formulation of flavor molecules in foods is important in almost all culinary practices. However, the presence of these flavor components alone is not sufficient to describe the perception of food flavor. Flavor molecules need to be delivered to the chemical senses during eating in order to create sensations and perceptions. Accordingly, the binding, release, and transport of these molecules are all important factors contributing to flavor perception. The flavor perceived during eating arises from a complex time-dependent pattern of releasing volatile and nonvolatile components from the food matrix, a process which has different characteristics for particular foods. Nonvolatile compounds may be dissolved in the saliva surrounding the taste receptors and stimulate the receptors cells by reversible binding to the gustatory receptor proteins. Volatile compounds are transported back up through the nasopharynx into the nasal cavity. The transport of volatiles is facilitated by mouth movements, swallowing and breathing, which allow air to be moved retronasally from the mouth to the nose. Besides the release in the mouth, the release of volatiles from residuals of the bolus left in the pharynx after swallowing is also an important pathway.

5.2. Matrix Interactions and Thermodynamic Aspects

Flavor release from a food during eating will only occur if the partition equilibrium between the gas-product phases is disturbed. An important factor is the horizontal movement of the tongue pressing and releasing the food from the palate during chewing. This process creates pressure differences and temporal generation of a "fresh" or new air-water surface area, thus stimulating the kinetics release of volatiles from the product phase to the gas phase.

The interaction of the components with the food matrix has a significant impact on the variation of flavors in foods. An important factor in the relation governing flavor perception is the relation between concentration in some solvent (oil or water) and equilibrium partial pressure of some aroma component. Due to the nonpolar character of most aroma volatiles even a small concentration in water will generate a relative large partial pressure, and thus, odor molecules can be considered as very volatile in foods with an aqueous character. On the contrary, when the solvent is oil, a larger concentration is needed to generate the same partial pressure. To our knowledge a detailed thermodynamic analysis of odor in water and oil in terms of the size Henry's law constant, partitioning coefficients, and nonideality is not available in the literature. The differences between interactions with oil

and water as solvents can be noted in the fact that the odor recognition threshold concentration in general is much higher in the case of oil as a solvent as compared to water. Many foods are dispersed systems containing both aqueous and lipid phases, and the effect of lipids content on flavor release will reduce the concentration of headspace volatiles, but removal of lipids in low-fat foods may also result in increased release.³⁰²

On top of a solvent-like interaction flavors may be bound to food components and, since only the free dissolved flavor molecules exert a vapor pressure, fixation of flavors can have a significant effect on flavor perception. An example of fixation is the embedding of flavor molecules in glassy materials, like candies and cereals. Certain flavor compounds, e.g., aldehydes, may also become covalently bound to proteins during storage. Other types of binding include physicochemical interactions such as van der Waals, hydrogen bonding, ionic bonding, and hydrophobic interactions in proteins and hydrophobic coils of carbohydrates. Relatively high levels of monosaccharides and salts increase the release of the less polar volatiles, a phenomenon attributed to as a 'salting out' effect. A higher serving temperature will generally shift equilibrium toward more gaseous odor as binding and solubilization reactions in general are exothermic reactions.

5.3. Transport of Volatiles and Kinetic Phenomena

Besides the interactions with the food components, kinetic aspects of the transport of volatiles from the food matrix to the aqueous or gas phases are important. Once the food has entered the mouth it becomes wetted by a thin layer of saliva. Even the fragments during chewing will be rapidly coated by saliva. Accordingly, the flavors in solid foods must be transported through the aqueous layer to the air. It is unlikely that simple diffusion alone accounts for the release through these respective phases, since the mastication disturbs diffusion gradients and generates new interfaces. Depending on whether the food is a liquid, semisolid, or solid, different transport mechanisms apply and some of them have been modeled from a kinetic viewpoint.^{303–305} A higher serving temperature will again favor a greater rate of release of odor and taste.

5.4. In Vivo Flavor Generation

Besides the flavor compounds present in the food matrix, enzyme activities in the mouth from both digestive enzymes in the saliva, those from micro-organisms and those present in the food as prepared, all play a significant role in the modification and generation of particular flavor components. Thiols like 2-furanmethanethiol found in coffee undergo rapid oxidation, leading to a change in the profile of volatiles entering the nose via the retronasal pathway. Similarly, esters are rapidly hydrolyzed by enzyme activities in saliva.^{306,307} Further, aldehydes may be formed during the mastication process by lipoxygenase activities. Therefore, characterization of aroma volatiles in foods does not necessarily reflect the volatiles stimulating the chemical senses during eating. Instrumental methods for measuring flavor release in the nose, such as ACPI-MS and PTR-MS, made it possible to evaluate such changes in the concentration of flavor components at low sensitivity and high selectivity in real time.³⁰⁸

There are many factors influencing the retronasal flavor release and delivery, some of which have been briefly presented here. It is a challenge within molecular gastronomy to bring the physicochemical principles into practice, designing particular flavor-delivery systems contributing to the quality and timing of the sensory experience of the dish.

5.5. Sensory Perception of Flavor: Complexity and Deliciousness

Even though we talk of "the taste of food", senses other than that of taste contribute significantly to the sensory experience we have when we eat food. The "taste" of an orange, for example, is a result of the integration, in higher areas of the brain, of taste, smell, and tactile signals. Besides the sense of taste, which begins when taste receptors on the tongue are stimulated with substances that give rise to the experience of sweetness, saltiness, sourness, bitterness, or umami; olfactory (smell), tactile (touch), and chemestesis (e.g., hotness) sensations all make major contributions to the "taste" of food.^{309,310} Indeed, the sense of smell is of crucial importance for the perception and enjoyment of food, as may easily be demonstrated by blocking its function while eating. If you simply pinch your nose (or better that of your partner) when eating, the overall flavor quickly fades away, leaving only a sensation of sweetness, sourness, etc. This is the reason why food loses its 'taste' when we are suffering a cold; the reduced flow of aroma molecules into the nose means we sample far less of the aroma compounds and so are not able to integrate the full flavor.

The sense of taste has five independent components (salty, sweet, sour, bitter, umami), but the sense of smell has many more dimensions. Humans have around 500 different receptor types in the nose, and these open up a very rich space of smell/aroma experiences.³¹¹ Further, the texture of food contributes greatly to our perception of its 'taste'. Perception of hardness, elasticity, viscosity, brittleness, etc., is made possible by the action of the sense of touch; in the context of food, texture perception is often referred to as "mouthfeel".^{311,312}

Some dishes completely lose their appeal without the perception of hotness (e.g., much of Thai and Indian cuisine). These sensations arise by stimulation of the trigeminal nerve (fifth cranial nerve).³¹³ The senses of vision and hearing are of lesser importance for the actual experience of a meal but can, via the expectations they bring about in the eater, influence how the meal is perceived.

The brain has a somewhat modular functional architecture, especially at the first processing steps toward extraction of information about the environment. Each of the senses has its own neural system in the brain, and only later along the chain of processing is there massive integration of signals from the different sensory systems.^{309,314} From a functional point of view the brain's tasks are often subdivided into categories of perception, cognition, emotion, and action. Each of the senses performs tasks from each category. Perception allows the perceiver to obtain knowledge about what is where and when. Cognition is responsible for higher mental states (e.g., rational thinking, planning), which are often of a kind that allow for introspection and consciousness. Even though some cognitive processes are embedded in each of the senses, they are much more central to the so-called "higher senses", vision and audition. Emotional processes, on the other hand, seem to be more central to the "lower senses" of taste, smell, touch, and chemestesis. Any judgment of the pleasantness or hedonic quality of a stimulus is of an emotional nature,

and such processes are central to the senses which are strongly involved in the perception and evaluation of foods and drinks. Emotional activity in these senses is of crucial importance for all animals and constitutes the drive to satisfy the most basic needs of living beings: food and sex.³¹⁵ It is therefore not surprising that man shares many of the neural structures responsible for emotional processes with evolutionarily older animals. Man's larger brain houses structures in the neocortex, which he does not share with other animals and allows for other feats, such as language. However, the important feature here is the fact that we share emotional neural structures with other animals. These structures are found in the limbic system in the midbrain and in a number of structures in the forebrain and basal ganglia (orbitofrontal cortex, striatum, and nucleus accumbens).

Reward mechanisms are emotional in nature, and these mechanisms might have evolved to guarantee engagement in behaviors important for survival. A varied energy supply is necessary for survival, and eating food in most cases leads to rewarding feelings and pleasure.^{316,317} Dopaminergic pathways in the brain, i.e., neural structures depending on dopamine as neurotransmitter, have long been known to be crucial for reward mechanisms.³¹⁸ Recently, however, a new neurology of reward has emerged in which reward is suggested to consist of distinguishable processes in separable neural substrates. In this account liking (emotion or affect) is separated from wanting (or motivation), each having explicit as well as implicit components. Explicit processes are subjectively aware to us, whereas implicit processes exert their influence without being conscious to us.^{319,320} Contrary to previous belief, the pleasure of eating palatable food is not mediated by dopamine but rather by opioid transmission in a neural network including the nucleus accumbens, ventral pallidum, parabrachial nucleus, and nucleus of the solitary tract. Wanting (appetite, incentive motivation), on the other hand, is suggested to rely on a dopaminergic system with projections from the ventral tegmental area to the nucleus accumbens and circuits involving areas in the amygdala and prefrontal cortex.³¹⁹ The distinction between liking and wanting was originally based on work on rodents,³¹⁹ but psychophysical and neuroimaging studies on humans support the distinction.^{320,321}

Since eating and drinking are crucial to survival the motivational mechanisms and rewards related to feeding are strong. It might therefore not be very surprising that the biological mechanisms of feeding and addiction overlap throughout evolutionary history. Work in rodents has demonstrated increases in dopamine in nucleus accumbens induced by food and by amphetamine. The dopamine response to the two types of stimulation are qualitatively identical, although the size of the response is an order of magnitude larger for amphetamine.³²² Similar results have been obtained from neuroimaging studies on humans.^{323,324} Besides dopaminergic systems, several cholinergic systems in the brain have been implicated in both food and drug intake.³²⁵

Eating leads to satiety and termination of a meal. Humans have a number of satiety mechanisms, all eventually controlled by the brain, but the classical homeostatic satiety mechanism begins with events in the gastrointestinal system. Homeostatic satiety is a biological negative feedback system that works much like a thermostat. Hunger is signaled by a number of hormonal substances such as ghrelin in the stomach and NPY, orexin, and AgRP in the hypothalamus.

Different nuclei in the hypothalamus are thought to control hunger and satiety and the associated relevant behaviors. Intake of food depresses the hunger signals and leads to an increase in satiety signals such as CCK, GLP-1, PYY, insulin, and leptin. Food intake cannot, however, be fully controlled by homeostatic regulatory circuits in the hypothalamus. If this were the case, we would not expect the average weight to have steadily increased in the western world for many years to an extent that in many countries one-half of the adult population is now overweight or obese (BMI > 25). Berthoud³¹⁷ has argued that human food intake control is guided by cognitive and emotional rather than metabolic aspects in the obesogenic environment of affluent societies. As he succinctly has stated "The mind wins over the metabolism in the present affluent food world".³¹⁷ This state of affairs is often referred to as "the obesity epidemic" and constitutes a serious problem to the individual suffering from obesity as well as severe challenges to society, both in terms of lost work years and escalating expenses to treat the effects of obesity.³¹⁷

The hypothalamic system, classically believed to control food intake, has an abundance of connections to other parts of the brain involved in sensory and reward processing, and evidence seems to suggest that these cortico-limbic processes can dominate the homeostatic regulatory circuits in the hypothalamus. A more precise understanding of the interactions between these different systems participating in the control of food intake is important and necessary for the development of behavioral strategies and pharmacological interventions to curb inappropriate food intake.³¹⁷

Besides the homeostatic satiety system humans possess so-called sensory-specific satiety mechanisms. Sensory-specific satiety denotes the decline in liking of a food eaten to satiety without effects on the appreciation on other foods.³⁴ An animal endowed with such mechanisms will tend to eat a varied diet, which in turn will counteract the risk of malnutrition. These mechanisms also highlight the importance of reward for food intake. Work to understand the neurobiological and psychological underpinnings of inappropriate eating will accordingly have importance for the endeavors to produce superb experiences and pleasure from meals and vice versa. In short, a better understanding of what it is in a meal that can cause people to experience great pleasure and how to physically and chemically transform the raw materials to arrive at such an end product may have much to contribute to the task of developing strategies to overcome the obesity epidemic.

Recent work has demonstrated that there are different types of sensory-specific satiety mechanisms. Some are product specific, some are product-category specific, and some are genuinely sensory specific, determined by basic sensory attributes such as sweetness, sourness, and fattiness. These insights can be used to guide the composition of meals put together to produce maximal satisfaction as well as meals which produce maximal satiety with the lowest amount of energy content. Neuroimaging work has also begun to delineate the underlying neural structures and mechanisms responsible for sensory-specific satiety and hedonic pleasure related to eating.³⁴ Closely connected to these efforts is work that has demonstrated the effects of hot spices (irritants like capsaicin, piperine) on metabolism as well as the feeling of satiety. Use of hot spices not only can increase the pleasure gained from meals but also can lead to higher metabolism and increased feelings of satiety.^{326,327} The foods we eat are

to a large extent determined by our preferences. Other factors such as price, social context, etc., are also important, but within boundaries set by these factors, we eat what we prefer or like.

Research has demonstrated that we are born with very few specific preferences.³²⁸ Newborn babies have a strong preference for sweet and fatty taste and a dislike for bitter taste. From a developmental point of view the preference for sweetness and fat facilitate breastfeeding. The dislike for bitter has been interpreted as an inborn defense against bitter-tasting toxic alkaloids in nature. Most people have to reach adulthood before they have learned to appreciate the bitter taste of beer, coffee, and many vegetables. Thus, besides these few examples, all other preferences are incidentally learned by being exposed to them in the food culture one is born into. Such a system allows man to be omnivorous and able to adapt to whatever edible materials are found in his environment. There are no differences between the nervous systems of different human races and cultures, but the different cultures have nevertheless developed radically different cuisines or food cultures based on what nature provides. This demonstrates quite clearly that food preferences are learned and not in born.

Learning starts in the fetal state³²⁹ and during breastfeeding³³⁰ and continues through childhood and later life. Conditioned learning, where an unconditioned stimulus (which is unconditionally appreciated) is paired with a conditioned stimulus, is an important mechanism in forming human preferences for foods.³³¹ Learning (and memory) plays a major role not only in forming preferences but also for choice behavior when preferences have been formed. Recent work on food memory has demonstrated that elderly people have as vivid memories of foodstuffs as young people in line with the incidental learning and implicit nature of the memories. These memories also seem to be based on a kind of “novelty detection”, where people are especially adept at detecting slight changes from a food stimulus they have previously been exposed to rather than determining that a presentation of the previous stimulus is indeed identical to the learned stimulus.^{332–335} Memories of stimuli and events are important to raise expectations and can have a strong influence on what is perceived and how it is hedonically evaluated, as exemplified in a neuroimaging study by De Araujo and Rolls, in which they demonstrate that one and the same chemical used as a smell stimulus activates different parts of the olfactory brain, depending on whether subjects are led to expect the smell of “cheddar cheese” or “body odor”.³³⁶

Learning and memory in the chemical senses, important for food behavior, might work very differently from learning and memory in the higher senses, vision and audition, and this might have important implications for how to produce foods that are either manufactured to give maximal pleasure or produced more with health concerns in mind.

What makes a particular meal pleasurable? As preferences are learned and we have our own idiosyncratically coded memories, we should not expect to come up with an “ultimate meal” which will appeal to members of all food cultures, but there might nevertheless be more fundamental underlying principles which determine what brings pleasure to humans. Unfolding of such principles will most likely require different physicochemical materials and processes in different food cultures, but there might be more fundamental determinants of what activates the reward systems in our brains the most.

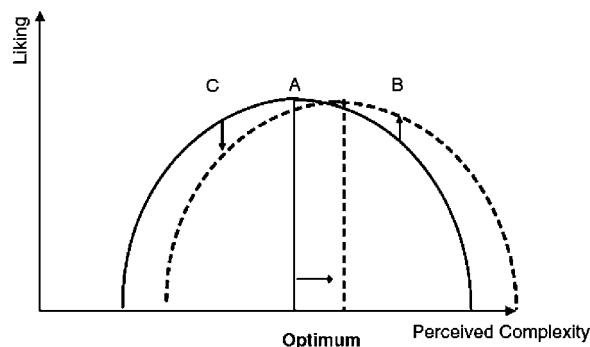


Figure 18. Inverted U relationship between liking and the arousal potential of a stimulus suggested by Berlyne’s arousal theory (solid curve), and the shift (broken curve) of the original inverted U curve and of the optimal individual level of psychological complexity upon exposure to a ‘Pacer’ (B).

Various lines of recent psychological and neuroscientific work suggest that this is indeed possible. Perceived complexity as defined by Berlyne^{337–339} is a general concept that has recently been applied to the study of (changes of) food appreciation.^{340–342} There is, in a very general sense, an inverted U relationship between “perceived complexity” and liking (of most stimuli) as shown in Figure 18. This is the case for rats, monkeys, and human beings. Perceived complexity is thus an important determinant of pleasure, and ongoing attempts to develop ways of quantifying it precisely are being performed.

Novelty seems to be another general concept which might be strongly related to reward.^{343,344} Recent neuroimaging findings indicate that midbrain regions preferentially respond to novelty and suggest that novelty can serve as its own reward.³⁴⁵ The mere anticipation of novelty seems to recruit reward systems.³⁴⁶ Novelty per se, of course, will not on its own guarantee a reward. It is easy to imagine novel foods which will generate a feeling of disgust rather than pleasure. Novel dishes with a clear relationship or reference to familiar dishes have in one recent experiment been shown to be appreciated more than those that do not.³⁴⁷

As an integral part of molecular gastronomy studies of, presumably universal, principles of how to join different sensations in space and time to obtain optimal pleasure are central. The application of physics and chemistry to the study of the soft but very complex materials that make up foods, in conjunction with modern psychophysical and neurophysiological studies of pleasure and satiety, could both contribute to a deeper understanding of human reward systems as well as to development of new foodstuffs that could bring more pleasure and healthier lifestyles to the eater.

6. Summary and the Future

For anyone who has read through all the preceding sections, it should be readily apparent that the overall effect of any individual foodstuff, let alone a complete dish or meal, is influenced by a diverse and complex set of factors that start with the production of the ingredients and via their processing, both physical and chemical, to produce aroma and tastant molecules as well as change the texture and color end as the food is eaten and digested with the sensations sent from all our senses to our brains, where we decide whether or not we enjoyed the experience and degree of pleasure imparted. Accordingly, if we are ever to be able to predict, a priori, how delicious a food might be, it will require

serious collaborative efforts from scientists of all the chemical (and other) disciplines.

As we have seen, some areas are much better understood than others. Some of the chemical reactions are generally well understood. Others, such as the Maillard reactions, are much less understood; although general schemes exist, the full details of these reactions still remain far too complex to permit any complete description. We will later in this section outline some of the major challenges which we believe are possible to tackle in the short term as well as lay out a potential long-term strategy for the future development of Molecular Gastronomy as a scientific discipline in its own right.

However, before we get carried away with grandiose schemes, we should return to a more basic and most important issue. We should address the question of why should the pursuit of all this research be worthwhile. Is Molecular Gastronomy necessary? To answer this question, we describe in the following sections a few aspects where MG may be able to make significant contributions in the near future. These range from questions that concern chefs and cooks, such as why do some food pairings enhance flavor while others can be quite unpleasant, to socially important issues such as how we might persuade people to adopt healthier diets and how we can encourage more youngsters to take up careers in the sciences.

6.1. Complexity and Satiety: Relationships between Liking, Quality, and Intake

It is obvious that the extent to which individuals enjoy the food they eat depends on a number of factors related to the food itself as well as their own individual set of experiences and memories. It is also clear that given choice and opportunity individuals will tend to eat that which they enjoy. Thus, it should be possible, if we can gain a better understanding of how enjoyment relates to the food preparation itself, to influence the diet of individuals in a positive, more healthy, fashion. There is no inherent reason why high palatability should necessarily lead to a larger intake. One can easily argue that it is the other way around: if eating is as much an activity engaged in to obtain pleasure as it is a means to secure the necessary energy intake, high palatability in a meal will lead to a smaller energy intake because sufficient satisfaction is obtained with smaller portion sizes. If this could be demonstrated in a number of cases, so that “quantity” could be replaced by “quality”, it may become possible to encourage more appropriate eating behavior in an environment with high food availability. More work to investigate the existing anecdotal evidence that we eat and drink less of high-quality products than we do of more mediocre products could indeed provide evidence for such a possible replacement of “quantity” with “quality”.

We think that Molecular Gastronomy is particularly well suited to make a contribution here because of the precise definition and high sensory quality of the foods we work with in Molecular Gastronomy. For example, particular sensory dimensions can be defined much more precisely by means of the methods used in Molecular Gastronomy. Experimenting with new physical and chemical methods which are used in Molecular Gastronomy kitchens and laboratories allows us to acquire many new insights about the individual senses' contribution to satisfaction and satiety. Along the way we will also need to develop new methods to quantify ‘satisfaction’, both psychophysically and neuro-

physiologically and by means of biochemical and neuropharmacological measurements. In this way one might hope that MG could also become a driver of development in the more psychological, neurological, and biochemical aspects of eating behavior.

One area of some immediate potential is the investigation of the relationship between food complexity and satiety. In particular, by using highly palatable, real, and complete meals, rather than the more usual simple single food (such as fruit juices or yogurts) approaches, we believe it should be possible to make a direct impact on food choice and intake.

Over the last 50 years the Western diet has changed enormously. For example, the British population eats less red meat, more poultry, and more processed food than 30 years ago. Although British Government statistics suggest that the consumption of fats, carbohydrates, and protein is falling and that of vegetable and fruit intake is increasing, there has still been a 10% rise in the incidence of obesity in the last 10 years.³⁴⁸ Data from the United States suggest that a key determinant in the increase in obesity is consumption of processed and “fast” foods; higher weight is associated with more food eaten away from home.³⁴⁹ In the United Kingdom about 30% of food expenditure is on food eaten outside the home. When eating out, people tend to consume larger portion sizes and more calories.³⁵⁰ Accordingly, we should ask are there opportunities for Molecular Gastronomy to provide routes to improved diet and consequently through that the health of individuals.

Foods vary tremendously in their energy density. During eating we need to predict how much food to consume in order to satisfy current and future short-term needs. One possibility is that meal size is governed by a simple feedback mechanism such as a gut hormone that is released or reaches a critical level when enough energy has been absorbed. However, the system needs to be more adaptable because meal termination occurs well before a significant proportion of food is emptied from the stomach for absorption.³⁵¹ In part, we overcome this problem by learning to predict the likely consequences of consuming individual foods (for a review, see ref 352). However, in addition to these food-specific associations, meal size also appears to be influenced by a range of other factors including food palatability,³⁵³ serving size,³⁵⁴ and the number of people present at a meal³⁵⁵ irrespective of the specific food that is being consumed.

Food complexity is not a straightforward concept and can be defined in many ways. If complexity is defined as the *sensory* experience, it might be argued that increasing flavor complexity could provide for increasing enjoyment and satiation. Conversely, it could be argued that highly processed foods, despite being potentially nutritionally less valuable, can also be extremely complex but in terms of their constituents rather than their flavors. For example, a simple pasta sauce prepared at home might contain olive oil, onion, garlic, tomato, tomato puree, and seasonings (salt, pepper, maybe some herbs), whereas a preprepared sauce might also contain sugar, modified maize starch, an acidity regulator such as citric acid, white wine vinegar, onion extract, and other nonspecified flavorings.

In addition to the potential effect of flavor or constituent complexity on food intake and satiety, there is an additional dimension to the sensory experience of eating that is textural complexity and palatability. Controlling for taste quality, a lessened desire to eat “hard” foods has been reported

following consumption of a “hard” lunch,³⁵⁶ and other work suggests that satiety can be affected by somatosensory features (texture, feel, quality) in addition to taste quality. It is not at all clear how different complexities in food may contribute to food intake and satiety.

On the basis of the above lines of evidence, it is at least possible that different aspects of food complexity play an important role in determining the satiating quality of foods and that the specific effect of complexity might be mediated via particular kinds of taste profiles. In recent years our affection for processed and manufactured foods has increased markedly. Yet, little is known about the complexity of these foods relative to ‘home prepared’ equivalents. By elucidating a role for complexity we may be better placed to explain the commonly held view that processed foods are overconsumed and regarded as unhealthy on this basis. Of course, this is a very simplistic approach to satiety and enjoyment of food; complexity is at best just one of many factors affecting our appreciation of the food we eat. Nevertheless, the role of sensory complexity has not been previously measured or explored with respect to pleasure, palatability, food intake, and satiety.

It is therefore clear that the links between sensory complexity, on the one hand, and pleasure, palatability, food intake, and satiety, on the other, are areas worthy of a proper scientific investigation. Such a study could be an excellent opportunity for Molecular Gastronomy to demonstrate a societal useful role.

6.2. Models for Cooks and Chefs

While there are some models already in the literature that attempt to describe the heat transfer in food as it cooks, these are not, in general, of much utility for the domestic cook or the chef in a restaurant. However, these people are those who are most often in need of simply and clear guidance on the optimum temperature and time to cook particular foods. This situation provides a wealth of opportunities for research with the objective of producing straightforward to use models that can be used in the kitchen. For example, we can envisage a computer package that provided with the dimensions, type, and cut of a piece of meat can suggest a range of different cooking methods (times and temperatures and even temperature profiles) that will give a range of different textures, colors, and flavors in the finished product. Such a tool could prove invaluable in any busy kitchen.

Such a system might be developed either from a purely theoretical standpoint or by a purely experimental approach. However, neither alone is likely to prove successful. The pure theory will find it hard to deal with the variability of meats, the different mass transport that will occur with different cuts, and the odd shapes and sizes of real pieces of meat. At the same time a purely empirical approach would involve the need to test such a large range of different examples that it is unlikely ever to provide for all the possible examples met in a real kitchen. It will only be through a combination of theory and experiment and collaborations between chefs and scientists working together that truly useful models and systems can be produced.

However, it is not only in the area of meat cookery that predictive cooking models can prove useful; the whole area of gels and gelation (under what conditions will the diverse range of food-approved gelling agents actually form gels, what properties will these gels have, and how stable will they remain) is another area that is ripe for development of

a detailed set of models. While much of this information is in the scientific literature, much is not and still needs to be discovered. For example, most phase diagrams of gelling systems are produced for just a single example of the gelling agent; other batches (or batches from a different source) are likely to have quite different molecular weights and distributions of molecular weights, making their gelling characteristics quite different. Formulating a schema which permits simple measurements (such as intrinsic viscosity) to be made and using these to predict gelling behavior in the kitchen would be another step forward.

Another area where MG may be able to contribute significantly and directly to the kitchen is that of food pairings. Chefs continually search for novel and interesting food and flavor combinations. Currently much of this work is hit and miss, although a number of empirical models have started to emerge and led to Web sites that offer suggested food pairings based on a concept of synergy between foods that contain similar components. It is interesting to note that here chefs are beginning to propose models that scientists should be able to test as MG develops.

Molecular gastronomy attempts to bridge the gaps between work in physics and chemistry over technology and food preparation to sensory perception and pleasure. Within this framework there is ample space to experiment with well-known (and less well-known) perceptual effects in space and time. Under this heading, studies of “flavor principles”, in the most general sense of the phrase, are of great interest. Why do some foodstuffs go well with some others but not all? What are the not well-understood chemical and perceptual principles underlying these phenomena? Do “flavor principles” transcend “food cultures”? Not such that the very same dishes should be highly appreciated all over the world but such that certain combinations of basic sensory perceptions would be enjoyed universally. Elucidation of these problems would not only be highly interesting from a scientific point of view but could potentially also make a major contribution to more appropriate eating behaviors worldwide.

6.3. Language of Sensory Properties: Engaging the Public

It is, however, not enough just to prepare food; we want to prepare the best and most delicious, nutritious, and healthy food we possibly can. However, how can we explain that the food really does taste good? How can we describe flavor? Is it possible to create a language of taste and flavor so that we understand how different people appreciate the same food differently? We have seen that the perception of flavor depends not only the taste and aroma molecules present in food but also on the way in which they are released in the mouth, which in turn depends on the individual eating the food.

These are all hard questions and involve not only the scientific community but importantly chefs, cooks, and of course the public at large. Here are opportunities to engage the public directly in research. In sensory science much progress has been made in naming food characteristics and finding descriptions and reference materials for sensory perceptions. Furthermore, many studies have been made to describe relationships between physical/chemical stimuli in foods and perceptions, although mainly under strict laboratory-controlled conditions in a sensory laboratory.

As we increase the communication between those who cook and those who are interested in the scientific basis of what happens as we cook (and consume) our food, so mutual benefits can arise. Chefs will persistently ask difficult questions that can lead to new research opportunities: why do some pairs of foods work so well together while others do not? Is there a way we can predict whether a particular pair of foods will make a “good” flavor combination or food pairing? The fact that chefs have asked this question has led some to hypothesize that if a pair of foods share similar aroma molecules they make good combinations in a dish. Although nothing more than a simple hypothesis, the concept has gained considerable approval within the gastronomy community; there are now several Web sites devoted to trying to suggest food pairings based on detailed analyses of the major aroma compounds found in the ingredients. However, there is no hard evidence for or against such a simple model; here then is another area ripe for proper research, research that of necessity would involve tasting some very fine foods indeed!

Then there is the question of how ingredients are perceived as being “natural” or “artificial”, such terms can have very different meanings to scientists and the general public. It seems obvious to most in the scientific community that if a food molecule is healthy to use and imparts desirable characteristics to a dish, then whether it is extracted from a fruit or synthesized in a laboratory should not matter at all. Here those practicing MG should perhaps engage with the public and help them understand that, for example, chocolate is a highly processed food that is far from the general public perception of a natural foodstuff “natural” while the much maligned and often perceived as “artificial” monosodium glutamate (E621) occurs naturally in a wide range of foods from mother’s milk and tomatoes to cheese.

6.4. Science Education Using Food as Exemplars

One area where Molecular Gastronomy is already having an impact is in schools. In the United Kingdom, chemistry classes now often take experimental examples from the world of food science. This has been much encouraged and enhanced as some of the finest chefs (especially Heston Blumenthal) have not only acknowledged the usefulness of chemistry in their own cooking but produced materials that can be used in schools. For example, the Royal Society of Chemistry has produced a text book for use in schools which draws heavily on a TV series “Kitchen Chemistry”, which was presented by Heston Blumenthal.

Current health and safety legislation often makes the use of “traditional” experiments in schools difficult, and many teachers are wary of using potential harmful chemicals in a school environment. However, foodstuffs are not seen as harmful chemicals, so that many reactions and processes can be demonstrated and even reproduced by pupils in a school laboratory. Returning chemistry in schools to a hands-on experience can only be a good thing.

The endorsement by celebrity chefs is a clear way forward for the engagement of youngsters with chemistry which sometimes is thought to be “boring”, “difficult”, and most importantly “uncool”. In the United Kingdom there is increasing, anecdotal evidence from schools that students are finding chemistry more approachable and distinctly “cool”.

Examples of the use of Molecular Gastronomy in school chemistry lessons include the following. The use of salt in cookery (illustrating boiling point elevation, titration, color

reactions, monovalent and divalent ions). Why do pans stick (providing an introduction to polymer chemistry and the structure of fats and oils)? The science of ice cream (illustrating the structure of ice and water and introducing concepts of enthalpy of fusion, nucleation, crystallization, and phase changes). It should remain an objective of Molecular Gastronomy research to retain the link to education and wherever possible develop more educational resources to encourage youngsters into the chemical sciences.

6.5. What Is Molecular Gastronomy? Where Will It End Up?

Finally, we should ask where Molecular Gastronomy might lead. Perhaps the most important objective of MG should be to delineate the essential principles that underpin our individual enjoyment of food. We hypothesize that there are a number of conditions that must be met before food becomes truly enjoyable, some trivial (e.g., the food should have some flavor), some very subtle (e.g., we may need to be in the “right frame of mind” to enjoy a meal), and many highly speculative (e.g., we may need a minimum number of different simultaneous or temporally related stimuli before a particular dish becomes interesting). The long-term aims of the science of MG should be to elucidate these minimal conditions, to find ways in which they can be met (through the production of raw materials, in the cooking process, and in the way in which the food is presented), and hence to be able to reasonably well predict whether a particular dish or meal would be delicious.

We can see many areas where MG can and should develop. For example, there are many traditional processes used by chefs in their kitchens. We can legitimately ask why do we do use these processes? Are they really the best possible methods or have they just been handed down from chef to apprentice over many decades without any real development or optimization? Such systematic and scientific studies of gastronomic procedures could form the basis for the rationalization and improvement of basic kitchen processes. Similarly, there are many classical dishes or components of dishes that have earned a reputation for excellence and remained on menus with little experimental development. A scientific study comparing classical dishes that have stood the test of time with historic dishes that have not may throw some useful light to help us understand why it is that some dishes do indeed achieve greatness and stand the test of time.

Another important aspect of Molecular Gastronomy and one that is much practiced by Dr. Herve This at INRA is the systematization of recipes or procedures. In a similar way to the systematization of sauces by This it should be possible to rationalize other processes. For example, the boiling of sugar solution is traditionally described in terms of “stages”, which could perhaps be rationalized using glass theory.

It may even become possible to give some quantitative measure of just how delicious a particular dish will be to a particular individual. Thus, in the future, we may be able to serve different variants of the same dish to our dinner party guests so that each has their own uniquely pleasing experience. If MG can achieve such a goal, it will go a long way to changing forever the public perception of chemistry.

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