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Ullmann's Food and Feed

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Preface

This handbook featuresselected articlesfromthe 7th edition of*ULLMANN'SEncyclopedia ofIndustrial Chemistry,* including newly written articles that have not been published in a printed edition before.

True to the tradition of the ULLMANN'S Encyclopedia, food and feed are addressed from an industrial perspective, including production figures, quality standards and patent protection issues where appropriate. Safety and environmental aspects which are a key concern for modern process industries are likewise considered.

More content on related topics can be found in the complete edition of the ULLMANN'S Encyclopedia.

About ULLMANN'S

ULLMANN'S Encyclopedia is the world's largest reference in applied chemistry, industrial chemistry, and chemical engineering. In its current edition, the Encyclopedia contains more than 30,000 pages, 15,000 tables, 25,000 figures, and innumerable literature sources and cross-references, offering a wealth of comprehensive and well-structured information on all facets of industrial chemistry.

1,100 major articles cover the following main areas:

- Agrochemicals
- Analytical Techniques
- Biochemistry and Biotechnology
- Chemical Reactions
- Dyes and Pigments
- Energy
- Environmental Protection and Industrial Safety
- Fat, Oil, Food and Feed, Cosmetics
- Inorganic Chemicals
- Materials
- Metals and Alloys
- Organic Chemicals
- Pharmaceuticals
- Polymers and Plastics
- Processes and Process Engineering
- Renewable Resources
- Special Topics

First published in 1914 by Professor Fritz Ullmann in Berlin, the *Enzyklopädie der Technischen Chemie* (as the German title read) quickly became the standard reference work in industrial chemistry. Generations of chemists have since relied on ULLMANN'S as their prime reference source. Three further German editions followed in 1928 – 1932, 1951 – 1970, and in 1972 – 1984. From 1985 to 1996, the 5th edition of ULLMANN'S Encyclopedia of Industrial Chemistry was the first edition to be published in English rather than German language. So far, two more complete English editions have been published in print; the $6th$ edition of 40 volumes in 2002, and the 7th edition in 2011, again comprising 40 volumes. In addition, a number of smaller topic-oriented editions have been published.

Since 1997, *ULLMANN'S Encyclopedia of Industrial Chemistry* has also been available in electronic format, first in a CD-ROM edition and, since 2000, in an enhanced online edition. Both electronic editionsfeature powerfulsearch and navigation functions as well asregular content updates.

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Symbols and Units

Symbols and units agree with SI standards (for conversion factors see page XI). The following list gives the most important symbols used in the encyclopedia. Articles with many specific units and symbols have a similar list before the references.

Symbols and Units (Continued from p. IX)

Symbol	Unit	Physical Quantity
U	J	internal energy
V	$m^3,$ L, mL, μL	volume
w		mass fraction
W	J	work
x_B		mole fraction of substance B
Ζ		proton number, atomic number
α		cubic expansion coefficient
α	$Wm^{-2}K^{-1}$	heat-transfer coefficient (heat-transfer number)
α		degree of dissociation of electrolyte
$[\alpha]$	10^{-2} deg cm ² g ⁻¹	specific rotation
η	Pa·s	dynamic viscosity
θ	C	temperature
χ		c_p/c_v
λ	$Wm^{-1}K^{-1}$	thermal conductivity
λ	nm, m	wavelength
μ		chemical potential
$\boldsymbol{\nu}$	$\text{Hz}, \text{ s}^{-1}$	frequency
$\boldsymbol{\nu}$	m^2/s	kinematic viscosity (η/Q)
π	Pa	osmotic pressure
Q	g/cm ³	density
σ	N/m	surface tension
τ	Pa $(N/m2)$	shear stress
φ		volume fraction
χ	Pa^{-1} (m ² /N)	compressibility

***The official unit of pressure is the pascal (Pa).

Conversion Factors

Powers of Ten

Abbreviations

The following is a list of the abbreviations used in the text. Common terms, the names of publications and institutions, and legal agreements are included along with their full identities. Other abbreviations will be defined wherever they first occur in an article. For further abbreviations, see page IX, Symbols and Units; page XVII, Frequently Cited Companies (Abbreviations), and page XVIII, Country Codes in patentreferences. The names of periodical publications are abbreviated exactly as done byChemical Abstracts Service.

Frequently Cited Companies (Abbreviations)

Country Codes

The following list contains a selection of standard country codes used in the patent references.

∗ ForEurope, FederalRepublic of Germany,Japan, and the Netherlands, the type of patent isspecified: EP (patent), EP-A (application), DE (patent), DE-OS (Offenlegungsschrift), DE-AS (Auslegeschrift), JP (patent), JP-Kokai (Kokai tokkyo koho), NL (patent), and NL-A (application).

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18

Periodic Table of Elements

element symbol, atomic number, and relative atomic mass (atomic weight)

1A "European" group designation and old IUPAC recommendation
1 group designation to 1986 IUPAC proposal
11 September 2001 provided proteined in the Chamical Abstracts Service until the end of 1986

^a provisional IUPAC symbol

* radioactive element; mass of most important isotope given.

Part I

Introduction

Foods, 1. Survey

W. FRANK SHIPE, Cornell University, Ithaca, New York 14853, United States

1. Introduction

Foods are mixtures of chemicals that are consumed by humans to satisfy their appetites for nourishment and pleasure. The nature and reactivity of the chemical constituents determine the properties of foods. The sensory properties, i.e., appearance, flavor, and texture, determine the acceptance of food and the pleasure derived from consuming it. Water-soluble components (salts, sugar, acids, and bitter substances) determine the taste, and volatile compounds determine the aroma. The texture is due to insoluble complexes or compounds such as proteins and polysaccharides; in some foods, lipids contribute to texture. Pigments are critical contributors to appearance. Most of the nutrients are provided by proteins, vitamins, and minerals, whereas carbohydrates and fats provide the energy. The ideal food should be both delicious and nutritious. Unfortunately, many nutritious foods are considered unappetizing by many people.

The following procedures or processes have been used to produce appealing, nutritious foods (for details, see \rightarrow Foods, 2. Food Technology):

1. *mixing products*, e.g., fruit salads, vegetable salads, and fruit yogurts

- 2. *adding seasonings or other materials*, e.g., adding soy protein to sausage or smoking meats
- 3. *fractionating* to produce new products, e.g., separating milk to yield cream and skim milk
- 4. *homogenizing* to produce a more uniform product, e.g., peanut butter or milk
- 5. *fermenting* and *pickling* to produce new and more stable products, e.g., cheese manufacture
- 6. *enzymatic treatment*, e.g., enzymatic modification of starch to produce corn syrups of varying sweetness
- 7. *thermal processing* including cooking and baking, to destroy undesirable microbes, enzymes, and antinutrients such as trypsin inhibitors and enhance sensory appeal.

2. History of Food Production and Preservation

In the beginning, foods were selected from available natural products [1–8]. This led to the development of regional eating habits. The

origin of modern economic plants was possibly as follows [1]:

At first, selection of food from the available supply was based primarily on sensory properties. By trial and error, people learned that some products satisfied their appetites while others adversely affected their health. The people who made the right choices lived to pass on the information to the next generation.

In the days when humans were merely hunters or gatherers of foods, the adequacy of diet depended on the types and quantity of available plants and animals. The need to develop methods for preserving food for use throughout the year became obvious. Concern over the quantity and quality of food increased as population increased. These food problems stimulated development of methods for producing and preserving foods $(\rightarrow$ Foods, 2. Food Technology). The progression of civilization from the food gathering stage to the early food production era, i.e., from the Old Stone Age to 400 AD, is shown in Table 1.

In Germany, substantial increases in agricultural production occurred after the introduction of the iron plow in the 6th century, the horseshoe in the 9th century, and the horsecollar soon after. The threefold rotation system (onethird of the land remained fallow, summer crops were raised on another third, and winter crops on the other third) also increased production.

Table [1](#page--1-0). History of growing, processing, and preserving food [1]

Date (approximate) Period	Food	Farming-trading	Preserving-processing	Scientific-technological advances
Prior to 15 000 BC Paleolithic (second period of Stone Age)	eggs, fish, fruits, honey, insects, nuts, seeds, roots, small animals		drying, pounding, roasting	bags, baskets, clothes, language, "made" fire, painting, sculpture, stone and bone implements
15 000 BC Mesolithic (transitional period of Stone Age)	bigger selection of food, storing berries and wild fruits		boiling, drying fish, smoking, steaming, storing food	bow and arrow; dog, goat, reindeer, and sheep (domesticated); claycovered baskets
9000 BC Neolithic (last period of Stone Age) villages	domesticated animals, milk, butter, cheese, gruel, dates, olives, grapes, beer, vinegar, wine	cultivating cereals (seasonal) in permanent fields using hoes and hand plows, pruning	alcoholic fermentation, adding acetic acid, salting, baking, making bread, sieving, pressing primitively, seasoning	pottery wheel; spinning; weaving; wood, flint, and bone sickles; saddle quern; mortar; fishing with hooks and nets
3500 BC Bronze cities	soybeans, figs, rice, olive oil, vegetables, lentils, cabbage, cucumbers, onions	irrigating, plowing with horses and oxen, much trading locally and externally	filtering, lactic acid fermentation, more types of flavoring, flotating, leavening bread, making sausage, frying, pressing (sophisticated and complex), clarifying	architecture, smelting, wheeled carts, ships, writing, bronze tools, mathematics, rotary millstones, bronze weapons, astronomy, shadoofs, medicine, chemistry
1500 BC Iron	artichokes, beans, fruits, lettuce, sauces, spices	trading by land and sea, using heavier plows	refinement of flavoring and cooking	pulleys, glass, improved and cheaper tools and weapons, currency
600 BC-400 AD Roman	sugarcane, apples, asparagus, beets, oranges	using reaping machines, rotating legumes, using plows with wheels, trading extensively	food adulteration common	water mills, donkey mills, wooden cooperage

Component	CAS registry number	Food	Investigator
Lactose	$[63-42-3]$	milk	F. BARTOLETTI (1586-1630)
Fructose	$[57-48-7]$	honey, raisins	J. R. GLAUBER (1604-1668)
Gluten	$[8002 - 80 - 0]$	flour	F. M. GRIMALDI (1618-1663)
Tartar, ethanol	$[868-14-4, 64-17-5]$	wine	J. D. PORTIUS (1636-1703)
Sucrose	$[57-50-1]$	beets	A. S. MARGGRAF (1709-1792)
Citric acid	[77-92-9]	lemon juice, gooseberries	C. W. SCHEELE (1742-1786)
Malic acid	$[6915-15-7]$	apples	
Glycerol	$[56-81-5]$	olive oil	

Table 2. Some components isolated from foods prior to 1800

During the *Middle Ages* the variety of available foods increased as a result of increased traveling and trading. The discovery of America had a pronounced effect on the variety of food with the introduction of potatoes and corn, as well as other native American products, such as tomatoes, peanuts, lima beans, and turkeys.

The 16th century marked the beginning of the so-called *Golden Age of Science* [\[1](#page--1-0)], [6–10]. During this time, scholars investigated the nature and composition of foods. Some of the components discovered are listed in Table 2. These discoveries gave credibility to the scientific approach to biological problems and stimulated further research and technical developments (Table 3).

In the *last two centuries* considerable progress has been made in increasing the quantity and improving the quality of food [11, 12].

Food Quantity. Quantitative increases in the food supply have resulted from the following:

- 1. The use of better breeding practices and careful genetic selection, which led to the development of high yielding varieties of wheat and rice.
- 2. Replacing draft animals with mechanical power increased the acreage that could be farmed and released millions of hectares of land that had been devoted to raising feed for horses. However, mechanization of agriculture increased fossil fuel consumption.
- 3. Irrigation has converted vast areas from desert or semidesert to profitable food producing areas. Unfortunately, continuous irrigation has caused water logging and increased soil salinity.
- 4. The use of chemical fertilizers has created remarkable increases in production $(\rightarrow$ Fertilizers, 1. General). The gains have been partially offset by the cost of the fertilizers in terms of dollars and expenditure of fossil fuel. In some cases the runoff of chemical

Table 3. Chronology of some developments in food technology

Date	Inventor	Process or product	Purpose
1679	PAPIN	digester	cooking in iron pot with clamped on lid
1809	N. APPERT	appertization	cooking in sealed glass jars
1810	N. APPERT	autoclave	cooking canned food under pressure
1830	A. COFFEY	Coffey still	continuous distillation
1830	N. RELLIEUX	triple effect evaporator	energy efficient evaporation
1835	SULZBERGER	roller milling	roller process for flour milling
1855	J. A. JUST	roller dryer	energy-efficient drying
1856	G. BORDEN	evaporated milk	milk evaporated under vacuum and packed in hermetically sealed cans
1860	F. CARRE	mechanical refrigerator	water-ammonia system for providing refrigeration
1865	L. PASTEUR	heat treatment	initially to preserve wine, then used to destroy pathogens in grape juice and milk
1874	A. K. SHRIVER	retort	closed kettle using super-heated or live steam for canning
1877	G. DE LAVAL	cream separator	rapid centrifugal separation of cream
1911	A. J. A. OTTESEN	quick freezing process	minimizing adverse effects on food during freezing
1920	K IDD $&$ West	controlled atmospheric storage	minimizing quality changes during storage of fruits
1931	C. BIRDSEYE	multiple freezer	energy-efficient freezing
1945	E. W. FLOSDORF	freeze-dryer	drying of frozen food under vacuum

fertilizers has polluted drinking water and increased the growth of algae in the streams, which has killed fish.

- 5. The use of pesticides has also contributed to the world food supply by eliminating pests that reduce yields or pests that consume harvested foods (\rightarrow Crop Protection). Because pesticides contribute to pollution and are hazardous to some species of animal life, alternative pest control methods have been and are being sought. Some success has been achieved in breeding disease-resistant varieties of plants and in developing biological methods, e.g.,microbial parasites, that destroy the pests.
- 6. Reduction in postharvest losses has been achieved by using storage facilities and packages that protect the food from biological, chemical, and physical damage $(\rightarrow$ Foods, 4. Packaging). In developing countries, postharvest losses can be as high as 50% for some commodities [13].
- 7. Recovery of foods and ingredients from underutilized products. For example, recovery of proteins from whey and blood [14–17], underutilized meats from chicken [18, 19] and fish [20, 21].

Food Quality. Much of the progress in solving food quality problems can be attributed to basic scientific studies that have identified the causes for changes in quality, e.g., LOUIS PAS-TEUR's studies, which led to pasteurization $(\rightarrow$ 3.7 Foods, 2. Food Technology). In the process of studying the mechanism of thermal destruction of microbes, researchers noted that in some cases thermal processing also affected flavor, color, and texture [\[6](#page--1-0)], [\[7](#page--1-0)], [22–24]. Heating fluid dairy products produced cooked (custardlike) flavor, which was found to be due to the release of sulfhydryl groups from proteins [25]. More drastic heating of milk or other foods containing carbonyl and amino groups caused both flavor and color changes. In 1908, A. R. LING described this reaction, and in 1912 L. C. MAILLARD investigated the mechanism [26]. Direct heating of products with high sugar content produced both caramel color and flavor. Heating affected the texture of meat and eggs by altering the proteins. It was found that the activity of

many endogenous food enzymes could be controlled by thermal processing [27], [28]. The importance and nature of enzymatic changes are discussed in Section 3.7 (\rightarrow Enzymes, 1. General).

Scientific studies have shown that many changes in food quality are due to either oxidative or hydrolytic reactions, and therefore, controlling them is important [6, 7, 29–31]. *Oxidative changes* have been minimized by (1) storing food in a controlled atmosphere, (2) using packages that are impervious to oxygen, (3) inactivating oxidative enzymes, (4) avoiding contamination with catalytic metals, or (5) addition of antioxidants (\rightarrow Antioxidants; → Foods, 3. Food Additives). *Hydrolytic changes* have been inhibited by (1) inactivating hydrolytic enzymes, (2) maintaining the integrity of cell walls or membranes, which protect the substrate, or (3) adding inhibitors [32].

3. Components and Their Reactions

Foods range in complexity from a single compound (e.g., sugar) to multicomponent mixtures (e.g., meat). The properties of foods reflect the properties of the individual components and their interactions. *Food interactions* include all types of noncovalent (van der Waals, hydrogen, ionic, and hydrophobic) and covalent bonds. These interactions contribute to a variety of structural features such as cell walls, micelles, fat globules, fat globule membranes, three-dimensional gel structures, muscle fibers, and curds.

The *reactions of components* in foods are affected by pH, temperature, concentration of reactants, available water, catalysts, activators, and inhibitors. They may be catalyzed by light, enzymes, and nonenzymatic materials such as metals. Inhibitors can be substances that chelate metal catalysts or that interact with one of the reactants. Chelating agents can react with calcium or iron and thus reduce their nutritional availability. The nutritional quality of foods can also be reduced by oxidation of essential fatty acids or other nutrients, or by the interaction of proteins with tannins. The optimal sensory and nutritional properties can be obtained by controlling the reactions of the components.

3.1. Water

Occurrence. Water [7732-18-5] is one of the basic and most ubiquitous constituents of living organisms, [6, 7, 33–36]. The water content of raw fruits, vegetables, and meats exceeds 50 wt %, but the concentration in cereals, nuts and many processed foods is lower (\rightarrow Foods, 2. Food Technology).

Water exists naturally as an intracellular or extracellular component in plants and animal products. It is used as a solvent for sugars, salts, and acids in some foods, as a dispersing medium for hydrophilic macromolecular carbohydrates or proteins, and as a dispersed phase in emulsified products such as butter and margarine.

Properties. Compared to other substances with similar molecular masses, water is unique $(\rightarrow$ Water, 1. Properties, Analysis, and Hydrological Cycle). Its ability to engage in threedimensional hydrogen bonding enables it to bond with organic molecules that contain nitrogen, oxygen, fluorine, or chlorine. The dissolution of sugar is because of bonding between water and the polar groups of the sugar. Dissolution of salts involves electrostatic forces between water and the positive ions which are greater than the attraction between ions.

Effect on Food. Water acts as a dispersing medium for amphipathic molecules, such as polar lipids, which have both hydrophilic and hydrophobic groups. The water associates with the hydrophilic moieties, such as phosphate groups, to "solubilize" the molecules. The amphipathic molecules form macromolecular aggregates, which are called micelles. Introducing hydrophobic substances, such as apolar groups of fatty acids, amino acids, and proteins, into water leads to an association of the apolar groups, i.e., hydrophobic interactions.

Water may be present in food as "free" water or "bound" water. *Free water* behaves like pure water, whereas the behavior of bound water is limited. *Bound water* has been defined as water that is not available as a solvent and does not freeze at -40 °C, although some scientists have suggested other definitions. The term "water binding" has been defined as the tendency of water to associate, with various degrees of tenacity, to hydrophilic substances. "Water-holding

capacity" has been used to describe the ability of a matrix of molecules to entrap a large amount of water in such a manner that exudation is prevented [\[7](#page--1-0)]. Although the entrapped water does not flow freely from the product, it behaves very much like pure water during processing. The water-holding capacity of meats and gels have a profound effect on rheological properties. The water-holding capacity of meats is affected by pH and salts, especially phosphates. A classification of water–protein thermodynamic associations is as follows [34]:

Structural water is water that is hydrogenbonded to specific groups; it participates in stabilization of structure and is unavailable for chemical reaction.

Hydrophobic hydration water is structured cagelike water surrounding apolar residues; like structural water, it is very much involved in stabilizing protein structure.

Monolayer water is the first adsorbed water monolayer; it is hydrogen-bonded and is unavailable as solvent, but may be available for chemical reactions; ranges from 4 to 9 g/100 g protein.

Unfreezable water includes roughly all water (structural monolayer, and perhaps some adsorbed multilayer water) that does not freeze at normal temperature; amounts to 0.3–0.5 g/g of protein and corresponds to water up to $a_w = 0.9$; amount varies with polar amino acid content and includes some water available for chemical reactions.

Capillary water is water that is held physically in clefts or by surface forces in the protein molecule (e.g., water entrapped in gels or cheese curd); its physical properties are similar to those of bulk water.

Hydrodynamic hydration water "loosely" surrounds the protein and is transported with the protein during diffusion (centrifugation); it has properties typical of normal water.

Water Activity [\[6](#page--1-0)]. A complete discussion of water activity can be found under \rightarrow Foods, 2. Food Technology.

Perishability. A general correlation exists between the perishability of food and water content, but a better correlation exists between perishability and water activity $(\rightarrow$ Foods, 2. Food Technology). Both enzymatic and nonenzymatic reactions tend to increase as water activity increases. However, enzymatic reactions are less sensitive to water activity changes. Nonenzymatic browning reactions reach a maximum rate at $a_w \approx 0.80$. Lipid oxidation is inhibited by increasing water content. Under some conditions water may form a protective film around the fat. The destruction of vitamin C and chlorophyll increases rapidly as the water activity increases. The rate of vitamin B_1 destruction reaches a maximum at $a_w \approx 0.5$ [\[7](#page--1-0)].

Food Quality. A complete discussion of the effect of freezing the water in food has on food quality can be found under \rightarrow Foods, 2. Food Technology.

3.2. Proteins (→ Amino Acids; → Proteins); [6, 7, 29, 37–44]

Structure. Proteins are polymers composed of amino acids linked together by peptide bonds. Proteins constitute ca. 50% of the dry matter of living cells and perform a vital role in the function and structure of the cells. Proteins containing only amino acids are called homoproteins, whereas those containing additional groups (i.e., prosthetic groups) are called heteroproteins. The heteroproteins include lipoproteins, glycoproteins, phosphoproteins, hemoproteins, metalloproteins, and nucleoproteins.

The complexity of proteins depends on the number and types of amino acids and other groups. The structural properties of some major food proteins are shown in Table 4.

Denaturation. The secondary and tertiary structures of proteins are fragile and, therefore, can be changed by a variety of treatments that do not cleave covalent bonds (with the exception of disulfide bonds). The term denaturation is applied to such processes. *Heating* is the most commonly used physical method for denaturing proteins. Most proteins are denatured or coagulated between 55 and 75 °C. The susceptibility of proteins to denaturation depends on the nature of the protein and environmental factors such as pH, water activity, ionic strength, and the types

of ions present. The proteins of egg white are readily denatured by heat, whereas casein and gelatin are relatively resistant. This resistance is attributed to the presence of high amounts of proline and hydroxyproline and low levels of sulfur-containing amino acids. Thermal denaturation of proteins can result in the following:

- 1. inactivation of enzymes
- 2. destruction of microbes
- 3. detoxification of toxic proteins
- 4. increased protein digestibility
- 5. improved texture of protein-rich foods
- 6. increased exposure of hydrophilic groups

The exposure of hydrophobic groups can cause changes in water and flavor-binding capacity and in solubility.

Physical treatments other than heating can also cause protein denaturation or other protein alterations. *Freezing and low-temperature storage* can cause aggregation and precipitation of some proteins (e.g., gliadin, 11 S soy proteins, and some egg and milk proteins). Aggregation refers to clustering of protein molecules or particles. In food systems, aggregation usually involves hydrophobic forces, but other forces may be involved in some cases. Precipitation involves separation of the protein from the rest of the solution or suspension. In some cases aggregation leads to precipitation. After freezing, fish may become tough and rubbery and lose moisture as a result of protein destabilization. Some *mechanical treatments*, such as the rolling and kneading of bread, may denature proteins. *High hydrostatic pressure* may also have a denaturing effect. Ovalbumin and trypsin have been reported to be denatured at pressures of 50 and 60 kPa, respectively [[7\]](#page--1-0). *Electromagnetic irradiation* can cause changes in the conformation of proteins. The extent of such changes depends on the wavelength and energy involved.

Proteins can also be denatured by *chemical reagents*. The structural stability of proteins is influenced by pH, with each protein having a characteristic stable range. Consequently, shifting the pH outside of this range with either acid or base denatures the protein. In some cases, native structure can be restored by readjusting the pH to within the stable range.