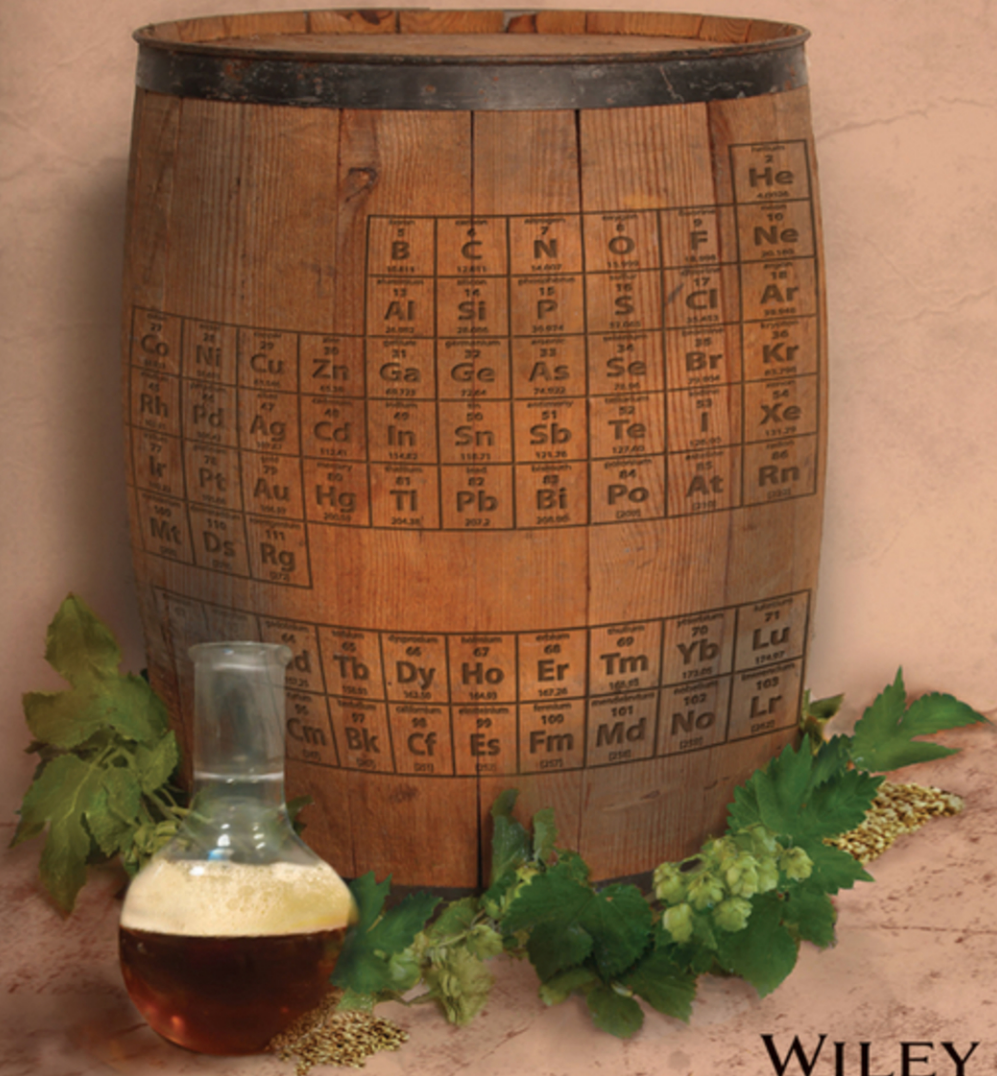
The Chemistry of BEER

The Science in the Suds

Roger Barth



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PREFACE

Whether you are a serious brewer or a person who is just interested in beer, the more you know about the scientific basis of beer, its preparation, and its flavors, the more you will appreciate and enjoy the depth and diversity of the world of beer. Although this book is written largely for the general reader, there is material that will be useful to brewers or people who are considering taking up brewing as homebrewers or as professionals. What distinguishes this book from others on the topic is the logic and sequence of the presentation of chemistry concepts, first atoms, then electrons, then chemical bonds, then molecules.

"Measurement in Chemistry," the Appendix to Chapter 3, includes units of measure, the mole concept, and mass calculations from chemical formulas. Water alkalinity and hardness measurements are dealt with in Chapter 4. Specific gravity tables and hydrometer corrections are presented in Chapter 10. The basics of computing a beer recipe are covered in Chapter 12. Chapter 16 includes some basic homebrewing recipes. Each chapter has references to some of the key primary and secondary literature and questions intended to help you study the material. Questions marked with an asterisk (*) are more challenging and may depend on supplemental material. Although commercial brewing and homebrewing are discussed to help give context to the material, this is not intended to be a complete textbook on brewing, several of which are mentioned in the chapter bibliographies. Nonetheless, it will be very helpful to read this book before one reads one of the brewing textbooks.

Many readers will be college students, some of whom are in the process of developing attitudes and practices regarding the use of alcohol. Alcohol is

what it is. It has enriched many lives and ruined many lives, making it much like every other aspect of the human experience. It should not be taken lightly. I hope this book will help its readers attain a thoughtful approach to alcohol. Those who are experiencing difficulties with alcohol should seek assistance from college, pastoral, or health counselors.

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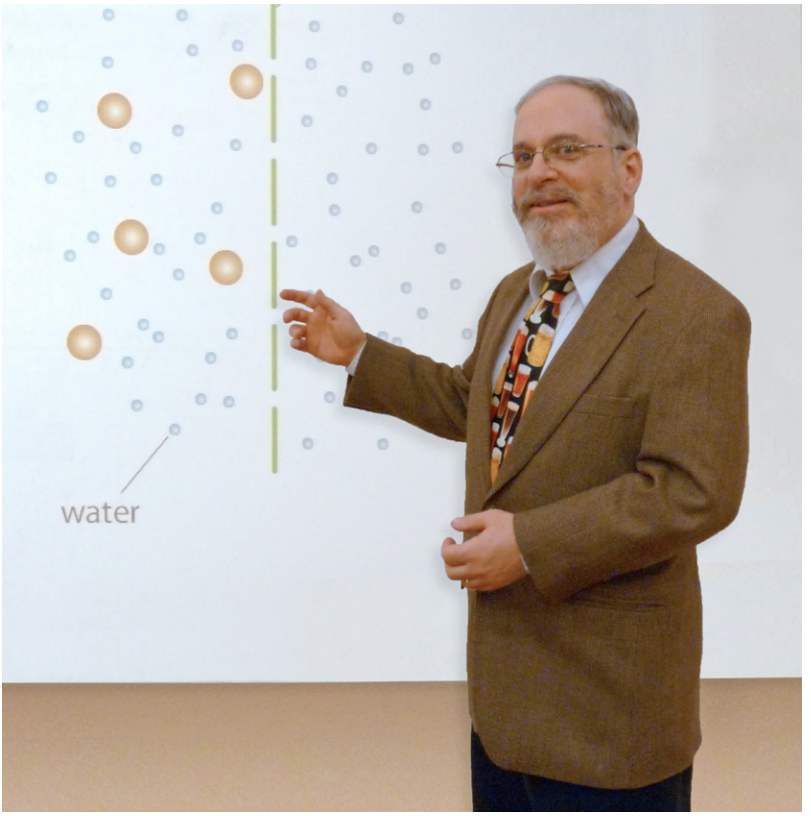
laboratory of this ultramodern facility. Fellow author Patrick McGovern (*Uncorking the Past*) provided valuable assistance for the first chapter, and Don Russell (*Joe Sixpack* column in the Philadelphia Daily News) suggested the subtitle of this book.

The visual appeal of this book is due to the artistry and skilled work of my talented wife, Marcy Barth. All photographs not credited to a specific source are hers. Her constant support made this project possible.

R. B.


water

ABOUT THE AUTHOR

Roger Barth was born in New York City. He attended public schools in Levittown, Pennsylvania, and received his bachelor's degree from La Salle College in Philadelphia. He was awarded a doctorate in physical chemistry at the Johns Hopkins University. After working at UOP Inc. in Des Plaines, Illinois, he did postdoctoral work at University of Delaware and at Drexel University. He has been teaching chemistry at West Chester University of Pennsylvania since 1985, and he created the Chemistry of Beer course in 2009.

Periodic Table of the Elements

1A	2A											3A	4A	5A	6A	7A	8A
1 H Hydrogen 1.008																	2 He Helium 4.003
3 Li Lithium 6.941	4 Be Beryllium 9.012											5 B Boron 10.811	6 C Carbon 12.011	7 N Nitrogen 14.007	8 O Oxygen 15.999	9 F Fluorine 18.998	10 Ne Neon 20.180
11 Na Sodium 22.990	12 Mg Magnesium 24.305											13 Al Aluminum 26.982	14 Si Silicon 28.086	15 P Phosphorus 30.974	16 S Sulfur 32.066	17 Cl Chlorine 35.453	18 Ar Argon 39.948
19 K Potassium 39.098	20 Ca Calcium 40.078	21 Sc Scandium 44.956	22 Ti Titanium 47.867	23 V Vanadium 50.942	24 Cr Chromium 51.996	25 Mn Manganese 54.938	26 Fe Iron 55.845	27 Co Cobalt 58.933	28 Ni Nickel 58.693	29 Cu Copper 63.546	30 Zn Zinc 65.38	31 Ga Gallium 69.723	32 Ge Germanium 72.61	33 As Arsenic 74.922	34 Se Selenium 78.96	35 Br Bromine 79.904	36 Kr Krypton 83.80
37 Rb Rubidium 85.468	38 Sr Strontium 87.62	39 Y Yttrium 88.906	40 Zr Zirconium 91.224	41 Nb Niobium 92.906	42 Mo Molybdenum 95.96	43 Tc Technetium [98]	44 Ru Ruthenium 101.07	45 Rh Rhodium 102.906	46 Pd Palladium 106.42	47 Ag Silver 107.868	48 Cd Cadmium 112.411	49 In Indium 114.818	50 Sn Tin 118.710	51 Sb Antimony 121.760	52 Te Tellurium 127.60	53 I Iodine 126.904	54 Xe Xenon 131.29
55 Cs Cesium 132.906	56 Ba Barium 137.327	57 La Lanthium 138.906	72 Hf Hafnium 178.49	73 Ta Tantalum 180.948	74 W Tungsten 183.84	75 Re Rhenium 186.207	76 Os Osmium 190.2	77 Ir Iridium 192.22	78 Pt Platinum 195.084	79 Au Gold 196.967	80 Hg Mercury 200.59	81 Tl Thallium 204.383	82 Pb Lead 207.2	83 Bi Bismuth 208.980	84 Po Polonium [209]	85 At Astatine [210]	86 Rn Radon [222]
87 Fr Francium [223]	88 Ra Radium [226]	89 Ac Actinium [227]	104 Rf Rutherfordium [265]	105 Db Dubnium [268]	106 Sg Seaborgium [271]	107 Bh Bohrium [270]	108 Hs Hassium [277]	109 Mt Meitnerium [276]	110 Ds Darmstadtium [281]	111 Rg Roentgenium [280]	112 Cn Copernicium [285]						

58 Ce Cerium 140.166	59 Pr Praseodymium 140.908	60 Nd Neodymium 144.242	61 Pm Promethium 144.91	62 Sm Samarium 150.36	63 Eu Europium 151.965	64 Gd Gadolinium 157.25	65 Tb Terbium 158.925	66 Dy Dysprosium 162.50	67 Ho Holmium 164.930	68 Er Erbium 167.26	69 Tm Thulium 168.934	70 Yb Ytterbium 173.054	71 Lu Lutetium 174.967
90 Th Thorium 232.038	91 Pa Protactinium 231.036	92 U Uranium 238.029	93 Np Neptunium [237]	94 Pu Plutonium [244]	95 Am Americium [243]	96 Cm Curium [247]	97 Bk Berkelium [247]	98 Cf Californium [251]	99 Es Einsteinium [252]	100 Fm Fermium [257]	101 Md Mendelevium [258]	102 No Nobelium [259]	103 Lr Lawrencium [262]

CHAPTER 1

INTRODUCTION

Beer! This foamy, refreshing, sparkling alcoholic beverage conjures images of parties, festivals, sporting events, and generally fun stuff. Beer is as much a symbol of our culture as football or ballet.

1.1 BRIEF HISTORY

Beer Origins

The origins of **beer** go back to the origins of civilization. Excavations at a prehistoric town, called **Godin Tepe**, located on the ancient Silk Road in the Zagros Mountains (Fig. 1.1) in what is now western Iran uncovered a 5500 year old pottery jar containing calcium oxalate (CaC_2O_4). Calcium oxalate is the signature of beer production. Although there is earlier evidence of mixed fermented beverages, the find at Godin Tepe is the earliest chemical evidence for the brewing of barley beer.

The history of beer is as old as history itself. History begins in **Sumer** (SOO mer), a civilization of city states in southeastern **Mesopotamia** (now Iraq) at the downstream end of the Tigris and Euphrates Rivers. Sumer is the site of the first known written language. Sumerian and other Mesopotamian languages were written with symbols, called **cuneiform**, made with a wedge-shaped stylus often pressed into moist clay tablets. Clay is durable; many ancient cuneiform documents survive and have been translated. Among the

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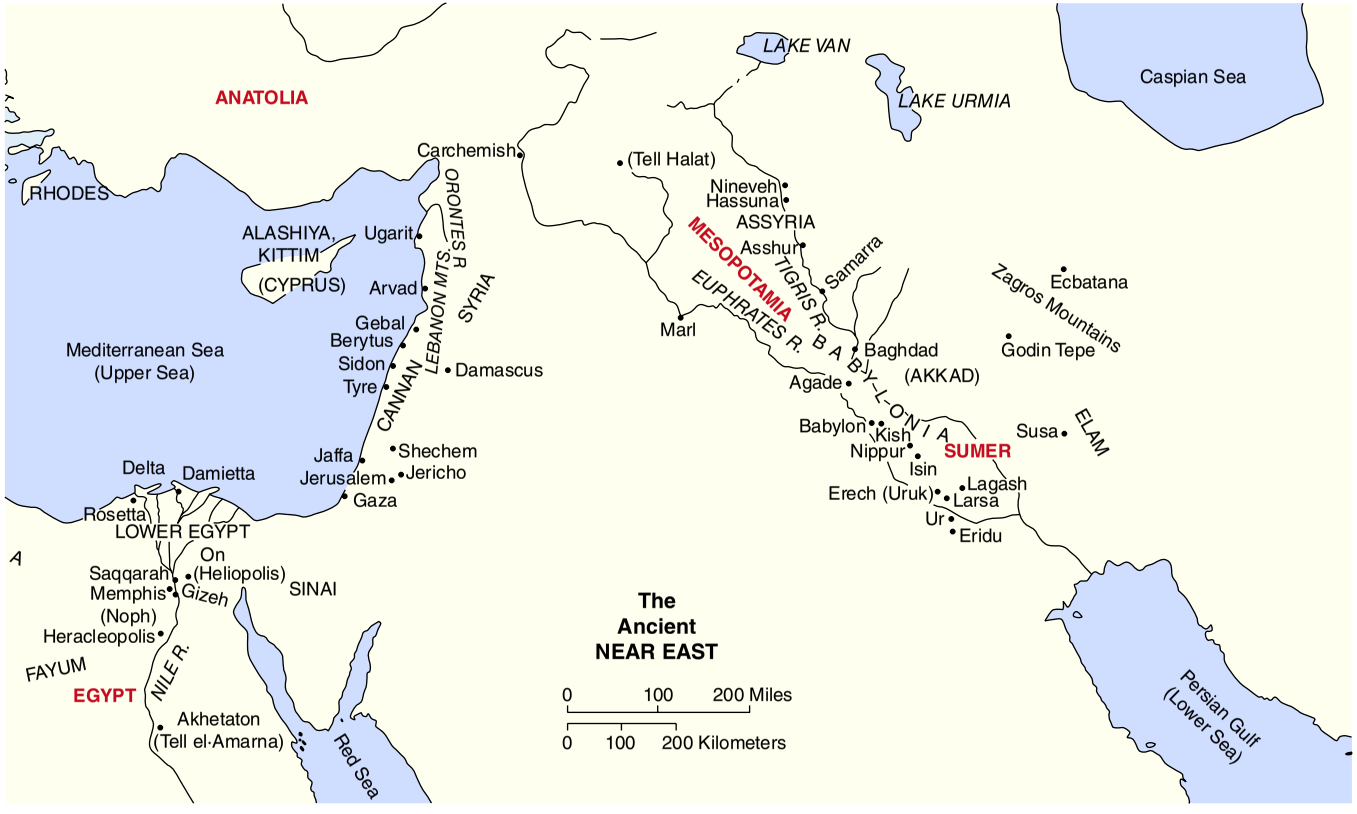

Figure 1.1 Map. *Source:* Adapted from CIA World Factbook. (See color insert.)

Figure 1.2 A 2600 year old Sumerian–Akkadian dictionary of brewing terms, Metropolitan Museum of Art, New York. (See color insert.)

earliest of these are documents written 5000 years ago concerning the brewing and consumption of beer (Fig. 1.2). These tablets record an already mature brewing culture, showing that beer was old when writing was new. One famous cuneiform tablet from 4000 years ago has a poem called *Hymn to Ninkasi*, a hymn of praise to the Sumerian goddess of beer. The *Hymn* has a poetic but not completely comprehensible account of how beer was made. The Sumerians made beer from bread and **malt** (or maybe malt bread), and flavored it, perhaps with honey. Sumerian documents mention beer frequently, especially in the context of temple supplies. Beer was also considered a suitable vehicle for administering medicinal herbs.

Babylon and Egypt

Dominance over the Mesopotamian region passed back and forth among the Sumerian cities until they were conquered by Hammurabi of **Babylon** 3700 years ago. Babylon was a city on the Euphrates upriver from Sumer. Beer made from barley or emmer (an ancient form of wheat) was a staple of the Babylonian diet. After Babylon came Assyria, ruling the Middle East from its two capitals of Assur and Nineva. The Assyrians were displaced by a

Figure 1.3 Ancient Egyptian tile: grinding grain to packaging beer, Carlsberg–Israel Visitor Center, Ashkelon, Israel. (See color insert.)

second wave of Babylonians, among whom was Nebuchadnezzar of Biblical infamy. These cultures continued the brewing tradition of Sumer. It is believed that brewing spread from the Mesopotamian region to Egypt, about 800 miles (1300 kilometers) away in Africa. Beer was the primary beverage in Egypt at all levels from the Pharaoh to the peasants. The dead were buried with supplies of beer. Mourners of deceased nobles brought offerings of beer to shrines in their tombs. There are many pictures and sculptures depicting brewing in ancient Egypt (Fig. 1.3). Modern scholars disagree on what can be inferred from these images about the details of ancient Egyptian brewing methods.

Europe

Little is known about the introduction of beer to northern Europe. Historical records from northern Europe before the Middle Ages are incomplete or missing. The **Neolithic** village of Skara Brae in the Orkney Islands off Scotland has yielded what some interpret as evidence of beer brewing 3500–4000 years ago. Finds of possible brewing 3000 miles from Sumer with little in between suggest that Europeans may have invented brewing independently. The Old English epic *Beowulf*, which was written some time around 1000, is set in a heroic Danish culture whose warriors seal their loyalty to their king during

elaborate feasting and drinking of beer and **mead**, an alcoholic beverage made from honey.

Monasteries

European **monasteries** played a key role in the development of modern beer. St. Benedict of Nursia (480–547) in Italy wrote a set of monastic rules providing for a daily ration of wine. Beer seems to have been permitted under the rules of St. Gildas (~504–570) in monasteries in Britain and Ireland. St. Columban (~559–615) may have been influenced by Gildas in providing beer for monks in monasteries he founded in France. The monastic customs came together when the synods in 816 and 817 at Aachen brought monasteries in most of Western Europe under a single set of rules. These rules provided that each monk would get a pint of beer or half a pint of wine a day. Monasteries ranged in size from 30 to as many as 400 monks with a similar number of servants and serfs. A monastery that served 150 pints of beer a day would need over 560 gallons (2100 liters) a month. The beer/wine ration assured that many monasteries outside of the grape growing regions would house large breweries. Monasteries served as guest houses for travelers and many sold beer to make extra income. In around 820 a detailed drawing was prepared for renovations of the Monastery of St. Gall in Switzerland. The plan shows three breweries, one near the monks' kitchen, one near the pilgrims' quarters, and one near the guest house. Although there is no indication that the three-brewery plan was actually realized, the St. Gall plan shows that brewing beer had become the norm for a northern European monastery. Starting perhaps in the middle 900s, some monasteries were able to maintain a beer monopoly by controlling the license to produce **gruit**, a mixture of herbs used to flavor beer. This practice waned by the fifteenth century, because **hops** replaced gruit in most regions.

Hops

The hop is a climbing plant whose flowers are used to flavor nearly all beer made today (Fig. 1.4). The first historical record of the use of hops in beer is in a list of rules for monks written in 822. The rules were written by the abbot Adalhard (751–827) for the Monastery of St. Peter and St. Stephen in Corbie, northern France. Adalhard also founded the Corvey Monastery in north central Germany; some sources get these two monasteries mixed up. Hopping of beer at nearby French monasteries in Fontenelle and St. Denis was recorded slightly later. Hops were not cultivated, but were gathered from the wild. The use of hops in beer spread slowly and irregularly throughout Europe. Early evidence of cultivation of hops dates from 859–875 at the Abbey of Freisingen in Bavaria, southern Germany.

The Hanseatic League was a confederacy of trading cities on the north coast of Europe from 1159 to the 1700s. The Hanse traded at North Sea and Baltic

Figure 1.4 Hops on trellis. (See color insert.)

Sea ports from Britain to Russia. One of the major Hanse commodities was beer. In its unhopped form, beer spoils rapidly, making it unsuitable for long distance trading. Hops, in addition to providing a unique flavor to beer, also acts as a preservative. Beer made with hops can stay fresh for weeks or months. The use of hops made beer a transportable commodity, allowing the Hanseatic League to introduce hopped beer to a large region in northern Europe. None of this happened overnight. Powerful people were making good money on gruit, the flavoring used before hops. These people used their influence on taxation and regulation to resist the introduction of a competing flavoring. Added to this is the innate conservatism of people about their food and drink. Hopped beer started to appear in England in the late 1300s mostly for the use of resident foreigners, including officials of the Hanseatic League. Different brewers made unhopped beer, called "ale" and the hopped product, called "beer." By the end of the 1600s all beer in England was hopped. Today we use "beer" as the general term and **ale** is contrasted to **lager** according to the fermentation temperature.

Commerce and Regulation

Starting in the later 1000s, commercial brewers began to set up shop in cities in what is now Belgium. Beer was an ideal product to tax because it was prepared in specialized facilities in batches of fixed size. While it might be possible to make a few pairs of shoes or rolls of wool under the table, it would have been difficult to conceal a batch of beer from the authorities. Beer taxation, both direct and indirect (as by taxing the ingredients), became an important source of revenue for various levels of government. Because of their financial interest in beer, governments got into the habit of regulating the ingredients, preparation, and sale of beer. In addition to taxation, other aspects of the brewing trade were of interest to the town government. Brewing requires heat, which in the Middle Ages meant fire. Breweries were subject to fires that, because of wooden construction, could spread to whole neighborhoods. In an effort to control fire risk, many towns had regulations on where breweries could be built and with what materials of construction. Brewing competes for grain with bread baking, which was seen as essential to feed the population. This may have been the motivation for the famous ***Reinheitsgebot*** (German: *Reinheit*, purity + *gebot*, order). This regulation, which permitted only barley, hops, and water in beer, was first issued in Munich in 1487. In 1516 the rule was extended to all of Bavaria (southern Germany). One effect of this regulation was a severe limitation on the import of beer into the regions in which it held sway. The *Reinheitsgebot,* in modified form, stayed in effect until it was set aside by the European Union in 1987. Even today it influences brewing practices all over the world.

1.2 THE WORLD OF BEER

Beer Consumption

Today, beer is the most popular alcoholic beverage in much of the world. In 2003, beer consumption in the United States was about 82 liters (231 cans) per adult. This may seem like a lot, but it ranks only eighth among the major beer consuming countries. The beer leader is the Czech Republic at 161 liters (464 cans) per adult. In 2008 the U.S. beer industry had revenues of 23 billion dollars and employed 27,000 workers. That makes beer a small but significant sector of the U.S. economy.

Varieties of Beer

We tend to think of beer in its northern European form. Standard American beer with its light color and clean, uncomplicated flavor belongs to a style called Pilsner lager, which is said to have first been marketed in Pilsen, Bohemia (now in the Czech Republic) on October 5, 1842. There are many styles of beer that are radically different from Pilsner lager. Just to name a few, there is ***chicha*** in

Central and South America, made with maize (corn); **opaque beer** in Africa, made with sorghum; ***sake*** (sa KEH) in Japan, made with rice; ***kvass*** in Russia and Eastern Europe, made from bread; and ***bouza*** in North Africa, made from bread and malt. These products are available in many local variations. Each is made by a unique process, and none tastes anything like Coors Light®.

Beer in Africa

Africa south of the Sahara Desert has an immense diversity of peoples, languages, natural resources, foods, and beer. European style barley beer is brewed and enjoyed in Africa; you may have heard of Tusker Lager®, a product of East Africa Breweries, Ltd. The real story of beer in Africa is in the many local styles using ingredients adapted to growing in the African climate. Beer is made with malt and unmalted flour, often including bananas to provide additional sugar. The grains may be millet (*Pennisetum glaucum*), sorghum (*Sorghum bicolor*), or maize (*Zea mays*, corn). Cloudy beer consumed while it is actively fermenting is called **opaque beer**. Some of these beer styles are produced commercially, for example, SABMiller brews an opaque beer called ***Chibuku***®. *Chibuku* is a maize or sorghum-based beer sold throughout southern Africa, often in waxed paper containers like those sometimes used for milk. A one-liter container costs the equivalent of 40¢. *Chibuku* is yeasty and sour and has a thick layer of sediment that is consumed with the beer. SABMiller characterizes *Chibuku* as "an acquired taste."

In some regions in Africa, beer is more than a beverage and social lubricant. In addition to its use at feasts and parties, beer is the focus of communal work projects. Beer is often perceived as a symbol of prosperity and generosity. Sharing beer can have significance that goes beyond ordinary hospitality. Serving or accepting beer can mark a person's position in the social order. Among the Gamo people of Ethiopia, it is a sign of distinction to be appointed as a *halaka*, a ritual-sacrificer. The appointee must be a wealthy, married, circumcised, morally upright male. Upon appointment, the *halaka* must sponsor two huge feasts at which as many as 300 people come to drink his beer.

Beer in Central and South America

There are many fermented beverages in Central and South America. Beer made from maize (corn) is called *chicha*. The maize can be sprouted and mashed much as Europeans make barley malt beer. Another process used in some areas is to moisten the ground maize with saliva. Enzymes in saliva allow starch from the maize to react with water to give sugar. The treated maize, called *muko*, is dried. When *chicha* is to be made, *muko* and some untreated ground maize are mixed with hot water and converted to sugar. After separation, the sugary liquid is boiled, chilled, and allowed to ferment in clay pots. Various regional styles of *chicha* are made using different varieties of maize and by flavoring the *chicha* with different fruits and spices.

Cauim and *masato* are fermented beverages made from manioc, the starchy root of the cassava shrub (*Manihot esculenta*). The raw roots must be boiled to remove toxic hydrogen cyanide (HCN). The boiled roots are chewed, allowing saliva enzymes to convert the starch to sugar. The chewed roots are boiled, and the sugary liquid is strained, chilled, and fermented.

Beer in the Far East

The best-known (to Westerners) type of beer from the Far East is *sake*, a Japanese beer made from rice (*Oryza sativa*). Related beverages include **huangjiu** from China, and **cheongiu** from Korea.

Sake is made by a unique process. Enzymes to convert the starch to sugar are provided by cultures of mold such as *koji* (*Aspergillus oryzae*), grown on steamed, highly polished rice. Yeast, water, and lactic acid are mixed in to make a starter. More steamed rice is added, and the mixture is allowed to ferment. Additional steamed rice and koji rice are added over a period of several days. At the end of the combined saccharification/fermentation, distilled (pure) alcohol may be added, allowing the product to be diluted with water for a smoother flavor. The *sake* is then pressed out through a filter and pasteurized. Aging can be prolonged.

There are as many styles of rice beer as there are of barley and wheat beer. Rice beer styles differ in the ethanol content, color, conditions of fermentation, degree of polishing of the rice, and sweetness or dryness of the *sake*.

1.3 BEER AND CHEMISTRY

Beer has played an important role in chemistry and biology both from a historical and from a technical point of view. Although many mistakenly attribute the discovery that beer yeast is a living organism to Louis Pasteur (1822–1895), it was reported nearly simultaneously by Charles Cagniard-Latour and Friedrich Traugott Kützing in 1837, and Theodor Schwann in 1839. This observation was strongly attacked by the leading chemists of the time, including Justus von Liebig (1803–1873). The mocking, dismissive tone of their attack seems more characteristic of political talk radio of our own time than scientific discourse. Liebig was eventually driven back from the position that yeast are not living, but to his death he opposed the idea that they are responsible and necessary for alcoholic fermentation. This bitter and fruitful scientific controversy over the nature of fermentation continued between Liebig and Pasteur, ushering in the modern age of biology. Liebig held that fermentation was a nonliving process in which the decaying matter contributed its energy to the breakdown of sugar. Pasteur held that fermentation was a part of the life processes of the microorganisms that were involved with it. The results and arguments of both men were hijacked by followers of the doctrines of **vitalism** and **mechanism**. The vitalists believed that the processes of life could never be explained by

the laws that govern ordinary matter. The mechanists believed that living systems follow the same laws as nonliving systems.

Now, 150 years later, we can say that Pasteur was right that all the fermentations that he, Liebig, and anyone else observed were caused by microorganisms. Liebig was right that fermentation is an ordinary chemical process that could, under the right conditions, occur without the participation of living cells. Eduard Buchner (1860–1917) proved this in 1897. Buchner ground up yeast in the presence of abrasives and squeezed out fluid through a cloth. When sugar was added to this fluid, carbon dioxide and alcohol were produced, exactly the same reaction as occurs in live yeast cells. Buchner won the Nobel Prize in chemistry in 1907, the first awarded for a biochemical discovery. In retrospect it is clear that Liebig and Pasteur did not allow themselves to be governed by doctrines like vitalism and mechanism. Pasteur was the first person to apply the principles of microbiology, a field he helped found, to the brewing of beer.

Many advances in chemistry were driven by the needs of the beer industry. These include measurement of temperature and of specific gravity. The Carlsberg Laboratory, set up in Copenhagen in 1875 (one year before Thomas Edison's laboratory in Menlo Park) as an arm of the Carlsberg brewery, was the site of several important discoveries. Emil Christian Hansen (1842–1908) was the first to raise up pure cultures of yeast (or any microorganism) on an industrial scale. The first reliable method of protein analysis was put forward by Johan Kjeldahl (1849–1900). The concept of pH, which is central to water chemistry, was introduced by S. P. L. Sorensen (1868–1939). The Guinness brewery in Dublin gave us the statistical method called **Student's t-test**, invented by William Sealy Gossett (1876–1937).

1.4 ALCOHOL AND PROHIBITION

One of the major reasons that people consume beer is because it contains alcohol. Alcohol, technically termed **ethanol**, is a **psychoactive** substance, which means that it changes the brain function. Depending on the dose, alcohol can lead to anything from mild **euphoria** to **stupor, coma**, and death. For some, alcohol is addictive. The alcohol content of beer, around 3–6%, is low enough so that a thirsty person can drink a glass without, in most cases, a severe effect on his or her ability to function. A similar quantity of wine, which has about three times the alcohol concentration, would be deleterious to one's coordination and judgment. The role of alcohol in society is complex and not altogether positive. One modern issue is the importance of cars in our culture and the problem of driving under the influence of alcohol. Not all such problems are new. Regulations on alcohol are documented in the **Code of Hammurabi** around 3800 years ago in Babylon.

The United States, in its brief history, has embraced and rejected alcohol, often simultaneously. The first English and European settlers in America set