BULLETIN FOR THE HISTORY OF CHEMISTRY

F. F. Runge

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The Cover…F. F. Runge in a porcelain imprint (Königliche Porzellanmanufaktur, Berlin, 1845) ….See page 30.

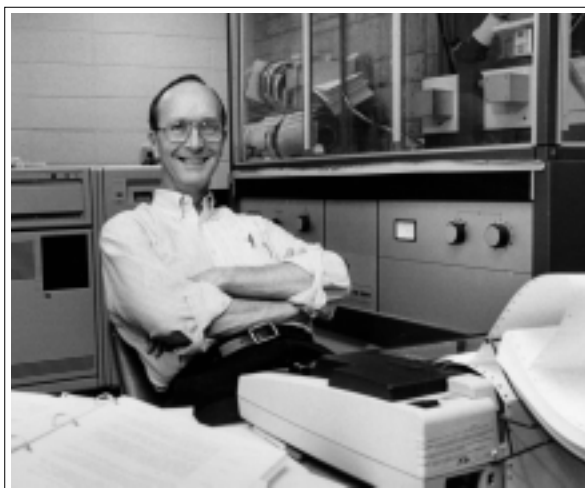# THE 2004 EDELSTEIN AWARD ADDRESS

THE DEEP HISTORY OF CHEMISTRY

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Introduction

Chemistry began long before Dalton or the alchemists, and even long before the earliest written chemical records such as those of the Roman, Pliny the Elder. In fact, chemistry was an essential component in the emergence of the human race and the development of human culture. These events took place during the last million years, reaching a climax in Southwest Asia some five thousand years ago.

J. B. Lambert

    In the development of human culture, physics preceded chemistry, if one defines tool making as involving the principles of physics. In 1949, Kenneth Oakley of the British Museum argued that tools in essence made our ancestors human (1). He argued that the process of tool making aided the evolution of a larger brain. Humans, however, are not alone in the physical processing of tools. Although many animal species use tools, their production almost always is controlled genetically. Nonetheless, learned, as opposed to genetically hard-wired, use of tools is not infrequent in the animal kingdom. Otters break open shell fish with rocks and crows drop bones from a height to open them. Some birds have proceeded to the next higher step, of manipulating the raw materials, as in adjusting the length of a stick to rout out insects from a log or nest.

    The earliest example of tool making by hominids (human-like animals in general, now often called hominins) at present is considered to be the altering of stones. Softer materials such as wood may have been worked previously, but the artifacts have not survived. Relatively sophisticated stone working by hominids (compared with the accomplishments of any non-hominid species) goes back at least 2.6 million years, the date of a site in Ethiopia (2). The species associated with this site is from the genus *Australopithecus*, an ape-like animal that preceded our genus *Homo*, for which the earliest date is 2.4 million years ago. Thus the physics of tool making was known to a very distant, pre-human ancestor.

The First Chemical Reaction

When did chemistry begin? The controlled production of fire was the first chemical reaction carried out by hominids. This discovery set hominids even further apart from other animals. Although a few species have made and worked crude tools, no other species has been able to create and control fire. If tool making set pre-hu-

mans on the road towards humanness (although other factors may have been at least as important), fire making confirmed, refined, and expanded the process, possibly helping to define the evolutionary moment when our ancestors became human. We became the first and only chemical animal. The control of fire had profound repercussions on our species. It provided protection and warmth, allowing our ancestors to migrate into cold climates and people the earth. Its light allowed them to extend their productive hours beyond daylight, expanding social interactions and helping the development of culture. In due course, fire was used to process food by stabilizing, tenderizing, and sterilizing it and possibly enhancing its taste. Such processing moves beyond survival strategies and becomes a cultural motif. Cooking itself of course is a chemical process. Another chemical process requiring fire was tool enhancement through annealing. Stone tools were hardened through heating tens of thousands of years ago. Finally, technologies utilizing fire ("pyrotechnologies") eventually included the production of ceramics, metals, and glass, as is discussed in later sections.

The earliest evidence for fire is controversial. Objects out of context may have been burned or charred for any number of reasons. The most unequivocal evidence then is the discovery of a hearth. The very presence of a hearth implies that humans were well advanced in the control of fire. The earliest such evidence may be at Terra Amata, located on the French Riviera, dated to at least 230,000 years ago (3). Humans living at this time were either very early examples of *Homo sapiens* or the predecessor species *Homo erectus*. Strong claims (but not a hearth) have been made for controlled fire at the site of Gesher Benot Ya'aqov in Israel, dating to 790,000 years ago, from the discovery of burned seeds, wood, and flint (4). Controlled fire was inferred from the pattern of distribution of these materials. The hominid species prevalent at that time was either *Homo erectus* or *Homo ergaster*. Observations at the even earlier site of Swartcrans Cave in South Africa and at a similar site in Kenya dating to 1-1.4 million years ago have been interpreted in terms of fire generated by hominid ancestors, either *Homo habilis* or *Australopithecus robustus* (5). The older evidence, however, is more controversial.

It is safe to conclude that some time between 230,000 and a million years ago, humans or their immediate ancestors had figured out how to create, control, and propagate fire as a tool, providing the many advantages described above and thereby making them chemists.

The Next Steps

The physical evolution of the modern human was almost complete by 100,000 years ago. Mental capabilities, as judged by the size and shape of the cranium, also were almost indistinguishable from that of modern humans. The extent of self consciousness in these peoples, however, is unknown. The development of speech undoubtedly was the critical step in establishing full humanness. This step required a modern larynx, not possessed by the Neandertals (*Homo neanderthalensis*). Speech arose as a means of communication possibly as early as 80,000 years ago but certainly by 35,000 years ago, probably in Southwest Asia and soon thereafter in Europe (6). Already before language, humans had employed a number of chemical processes and materials in addition to fire in its support roles.

(1) Cooking of food began more than 100,000 years ago, probably the result of observations on wildlife killed by natural fires (7). Although cooking is a chemical process, it is very complex and not easily attributed to one or more chemical reactions.

(2) Heat from fire also was used to improve the workability of flint and other stones, as early as 50,000 years ago. Heating stone up to about 350ºC prior to working improves its knapping and flaking properties. Heat treatment causes a color change in the stone as the result of molecular alterations, which may be studied by electron spin resonance spectroscopy (8).

(3) Natural pigments, particularly red ocher (hematite, or Fe_2O_3) were exploited by humans more than 100,000 years ago (9). Both Neandertals and Cro-Magnon peoples used such materials in burial or fertility rites. By 30,000 years ago, humans were grinding minerals to produce such pigments without chemical processing. In addition to reds and browns from red ocher, they obtained yellow from yellow ocher, black from soot or manganese dioxide, and white from calcined bone or white clays such as kaolin. These pigments were employed in the extraordinary cave paintings in southwestern Europe that date to more than 30,000 years ago (10).

(4) The chemical repertory of humans expanded into petroleum products. Bitumen was obtained from natu-

ral sites, of which the La Brea Tar Pits in Los Angeles is probably the most familiar to American audiences. Neandertals at the Mousterian sites of Umm el Tlel and Hummal in Syria left stone tools with bitumen residues that presumably had been used as adhesives as early as 36,000 years ago (11). Processing of bitumen involved mixing it with other materials to create something not readily available in nature: real chemistry. The addition of calcite ($CaCO_3$), silica (SiO_2), or gypsum ($CaSO_4$) to bitumen makes asphalt. Both pure and processed bitumen saw increased use in Mesopotamia from the residents of Jarmo in Iraq (7000 B.C.), the 'Ubaids (from 4500 B.C.), the Sumerians (from 3000 B.C.), the Babylonians (from 2000 B.C.), the Assyrians, and the Akkadians (12). These materials were used not only as adhesives but also as sealants for houses and boats and even as building materials. The Babylonians probably represent the high point of construction with bitumen, either as a constituent of bricks or as an adhesive between them, to construct roads, palaces, dams, bridges, sewers, and the famous ziggurats now in Iraq. Extant writings by Nebuchadnezzar II (ca. 630-ca. 561 B.C.) describe the use of bitumen in the Tower of Babel (the word being the Hebrew corruption of the name Babylon).

Synthetic Stone

Aside from the reworking of stone and food with fire, the aforementioned uses of chemical materials involved only physical, rather than chemical, processing. Thus, pigments were gathered from the environment but not altered chemically; bitumen was harvested from natural sources and possibly mixed physically with gravel. The working of stone, wood, bone, and other available raw materials involved physical processing only, albeit sometimes highly complex or artistic. In all these cases (except cooked food and heat-treated stone), the product clearly possessed the same chemical makeup as the raw materials.

What then was the most likely first example of human qua chemist? It may well have been the invention of plaster, to provide a manipulable substitute for stone. The very earliest suggestion of such a material occurred in the Sinai Peninsular at the site of Lagama North VII. At around 14,000 years ago, the inhabitants attached stone tools to handles by means of plaster. The invention of lime plaster has been attributed to the Geometric Kebaran culture of North Africa and Southwestern Asia during the Mesolithic or Epi-Paleolithic period (ca. 12,000-10,000 B.C.) (13). The Natufian culture (10,300-

8500 B.C.) succeeded the Kebaran in the Levant along the eastern coast of the Mediterranean Sea and utilized lime plaster extensively, primarily for architectural applications such as covering walls and floors. By the Pre-Pottery Neolithic Period (7500-6000 B.C.), as in 'Ain Ghazal in Jordan and Jericho in Palestine, architectural plaster was in wide use, and nonarchitectural uses such as fabricating vessels and ornamental objects were appearing. By 4000 B.C., the Egyptians were using both lime and gypsum plaster as mortar to bind construction blocks together.

Pre-pottery societies in the eastern Mediterranean thus had an extensive plaster technology, even by 6500 B.C. Production of plaster required the heating of either limestone or gypsum. Above 800°C, limestone ($CaCO_3$) loses carbon dioxide to form lime or quicklime (CaO). Addition of water to lime creates slaked lime, $Ca(OH)_2$, which upon application to a surface reabsorbs carbon dioxide from the atmosphere to revert back to calcium carbonate. At a lower temperature (150-200°C) gypsum (hydrated $CaSO_4$) loses most of its hydration to form dry plaster of paris, which requires only the addition of water to form the pasty mix that may be applied to a surface and allowed to dry to form hard, rehydrated gypsum. Lime plaster tended to be used in pre-pottery cultures of Anatolia and the Levant (roughly, modern Turkey and the eastern shore of the Mediterranean), whereas gypsum plaster was used in Mesopotamia (the land between the Tigris and Euphrates Rivers, roughly parts of modern Iraq and Syria). Plaster production was very energy intensive, and the energy source was timber for fuel. The loss of such resources in the Levant may have been contributory to the abandonment of settlements after 6500 B.C.

These are real chemical processes, involving manipulation of carbon dioxide and water content to control physical properties. Plaster provided a raw material that could transform pebbles into large stones of a desired size and shape, it could provide a smooth architectural surface, or it could serve as a bonding agent (mortar) between other materials. This technology predated pottery, glass, and metal production. During the period 14,000 to 6500 B.C., the chemical industry of plaster had become a major contributor to the culture of the region that has been called the cradle of Western Civilization, as plants and animals were being domesticated and as hunter gatherers were creating permanent settlements.

Ceramics

At some distant time, very creative humans made the connection between the effects of fire on clay and the accidentally hardened objects that they must have observed in the residues of fires. The first evidence for such activities has been found in Moravia in the Czech Republic (14). The site of Dolni Vestonice near Brno yielded a small (4.5-inch-tall) figurine of a woman with broad hips and pendulous breasts, one of many examples from Central Europe of the so-called Venus figurines from the Gravettian culture, 30,000 to 22,000 years ago. What sets the Venus of Dolni Vestonice apart is that it was made of fired clay, whereas all the other surviving Venuses were carved from stone, ivory, or bone. Moreover, the Moravian site contained two kilns and over 7000 ceramic fragments. These people clearly had discovered that fired clay had special properties, which they exploited entirely for artistic purposes. There is no evidence for utilitarian pieces such as ceramic vessels. The discovery in fact may have been a technological dead end, as no further examples of fired clay occurred for many millennia.

Wet clay possesses the remarkable properties of being able to be shaped (plasticity) and then to hold that shape upon drying (15). The resulting objects, however, are brittle and quickly crumble away. Such objects have rarely survived from antiquity. The third and most remarkable property of clay is its response to heating. Clay is composed of a silicate (Si-O) matrix in which many of the silicon atoms have been replaced by aluminum (hence, aluminosilicate). On heating to above about 600ºC, this lattice irreversibly loses molecules of water that were inherent parts of the original structure. The resulting dehydrated structure is permanently hardened. Above about 850ºC, further changes occur, called vitrification because of the smoothing effect it has on the material. As the temperature increases, the strength increases and the porosity decreases, making a more useful object. The material is termed earthenware when produced from the range 900-1100ºC and stoneware from the range 1200-1300ºC. Porcelain requires an even higher temperature, as well as a special type of raw material mix. All these materials are varieties of pottery and examples of ceramics. The latter term further applies to other materials produced by heating, such as bricks, tiles, or small ornamental objects such as the Gravettian Venus.

The discovery of pottery was driven by the utility of the products, which for the most part were vessels to hold solids and liquids. Materials could be stored, cooked, and transported in these vessels. The earliest archaeological records of pottery have been found in Japan, dating back as early as 14,000 B.C. The sites of Kamino and Odai Yamamoto on Honshu and the Fukui and Sempukuji Caves on Kyushu have yielded these extraordinarily early examples of pottery, corresponding to the Incipient Jomon period, or even earlier. Evidence for pottery in China and the Russian Far East was either contemporaneous or followed soon thereafter (if one considers a millennium or two "soon"). Pottery was well established and widespread in Eastern Asia at these early dates. The appearance of pottery in Western Civilization may have been an independent discovery or may have occurred by slow diffusion. It first appears at the sites of Çatalhöyük and Belbidi Cave in Anatolian Turkey, dating to 8500-8000 B.C. Certainly an independent discovery, pottery appeared in the New World during the period 2500-2000 B.C. in Ecuador, Colombia, Mexico, and the southeastern United States.

It should be noted that the raw materials of pottery involve more than clay and water. Substances formed from only these two constituents dry and harden on heating with structural shrinkage and cracking, so that the products are unstable. To circumvent this problem, early potters added a third component to the mix, called a temper or filler. Such a discovery was made throughout the world, with a wide variety of tempers, including sand, limestone, mica, straw, and dung (recall the Biblical bricks without straw). These materials not only enhance stability but also assist the process of vitrification. After the clay, temper, and water are mixed to form a paste, the object is shaped and allowed to dry before firing. Sometimes at this stage it is dipped into a very dilute suspension of the clay in water to provide a thin surface layer, called a slip, which smoothes the surface and creates a background for decoration. Alternatively, the object may be covered with a glaze for surface decoration. This glassy material may be fired at the same time as the clay or applied to the object after firing and then subjected to a second firing. Glazed pottery has been variously called majolica or faience.

Either the slip or the glaze can contain pigments to give color to the surface. The color of the clay itself is determined by several factors, including the specific elements present in the clay, the temperature at which it is fired, and the level of oxygen during firing. Normally the iron content creates reds and blacks. An excess of oxygen in the atmosphere (oxidizing conditions) gives rise to pink, red, or orange colors largely from the pres-

ence of Fe_2O_3. In the absence of oxygen (reducing conditions), blacks and grays occur, from either charred organics or reduced iron (FeO). High levels of calcium, when fired at 1100-1200°C, create a light-colored product termed creamware. At even higher temperatures, the white body of porcelain is formed, given the right kind of clay and temper.

Today the chemist can analyze every component of the pottery—clay, temper, slip, and glaze. The minerals present in the clay often can be determined by X-ray diffraction, the source of the clay by elemental analysis, the type of temper by optical microscopy, and the oxidizing nature of the atmosphere and possibly the firing temperature by Mössbauer spectroscopy. In this way the chemist can recreate the technology that originally gave rise to the product.

Metals and Metallurgy

The earliest worked material that has survived in the archaeological record is stone. Examples go back more than a million years to our predecessor species. The dominant worked material at a given time has given rise to the archaeologist's name for the period, in this case the Stone Age, divided into the Paleolithic (Old Stone Age) and Neolithic (New Stone Age, associated with farming and a settled existence). There may have been a Wood Age that preceded the Stone Age, as wood always was widely available and easily worked, but its instability during burial has left few remains but ashes. Certainly every available type of stone at some time was examined for the utility of its properties. On rare occasions, humans encountered stones that were plastic or malleable. On application of pressure, they altered their shape instead of chipping. These properties have obvious advantages. A damaged tool could be repaired by hammering. Moreover, new shapes could be created, such as flat sheets, which are impossible to achieve by chipping.

These malleable materials were native metals, mostly copper, silver, or gold. They were exceedingly rare and hence did not see widespread utilitarian applications. Copper normally is found in ores as the oxide or sulfide, materials that bear no obvious physical relationship to the native metals. The discovery of the relationship between copper ores and copper metal must be considered one of the most significant in human history (16). It probably occurred either as the result of heat treatment of stones or the use of stones in hearths or pottery kilns. The earliest evidence for the extraction of elemental metal from oxygen or sulfide ores, the process of smelting, has been found at the site of Çatalhöyük in Anatolia (Turkey) during the period 7000-6000 B.C. Although there was increased incidence of copper in the archaeological record at this time, metallurgy was only a peripheral industry for several thousand more years. The problem was that copper metal is relatively soft and hence not so useful for many tools. By the fourth millennium B.C. there was sufficient production of copper to warrant naming the period of the culture the Chalcolithic (Copper Stone) Age, intermediate between the Neolithic and Bronze Ages.

The second major metallurgical discovering was the mixing of metals to form alloys. The presence of a second metal produced a new material that was harder and less brittle than native metal: bronze. The first admixture with copper contained arsenic (arsenical bronze), possibly as the result of the use of arsenic-containing copper ores. Tin emerged as the additive of choice in the Old World during the millennium 4000-3000 B.C., the Early Bronze Age. The full flowering of the Bronze Age in the eastern Mediterranean was 3000-1200 B.C. or so. There has been a longstanding question in archaeology as to the source of tin for the Bronze Age. The ample tin mines of China and South America of course were not available, and the famous mines of Cornwall and Spain were not to be discovered until after 1000 B.C. Recent evidence has indicated that tin was mined in Turkey at the right period of time to help initiate the Bronze Age (17). Ancient peoples experimented with many other alloys, including brass (copper-zinc) especially in India, leaded bronze (copper-tin-lead) favored by the Romans, electrum (gold-silver) in the eastern Mediterranean, and tumbaga (copper-gold-silver) in the New World.

Some time during the second millennium B.C., iron began replacing copper for tools and weapons in the Mediterranean world. The change may have been brought about for a combination of reasons: shortages of the raw materials for bronze, appreciation of the superior properties of iron, or the economic advantage of the wide availability of iron ore raw materials. As with copper ores, iron ores had to be smelted. The Iron Age could not begin until this technology was well worked out. After 1500 B.C., the Hittite people in the Anatolian peninsula were using iron tools and weapons extensively. By 1200 B.C., the traditional transition point between the Bronze and Iron Ages, the Hittites had learned to alloy iron with carbon to produce steel. After 1000 B.C., as the Hittite culture declined, iron technology diffused

westward to the Hallstatt culture of central and western Europe and eventually to Britain by about 500 B.C. Thus the Iron Age began at different times for different places. Possibly independent discoveries of iron technology occurred during the Shang Dynasty in China before 500 B.C. and by the Nok culture in Nigeria by 400 B.C. It was never discovered in the New World.

It is worth noting that the ages of humanity (Stone Age, Copper Age, Bronze Age, and Iron Age) are named after the chemical substances that dominated the technology of the period. Chemistry was helping to define culture.

The archaeological chemist today analyzes metal artifacts to determine the nature of the alloy (18). Trace elements or isotope ratios may indicate the source of the metal ore or the authenticity of the artifact. The profile of trace elements in native copper has been used widely as a means to determine the sources of copper ores on a worldwide basis (19). The ratios of lead isotopes are similarly useful in determining the source of lead. The level of gold impurities in silver coins has been used as a test for authenticity. Modern refined silver is much purer than ancient silver. Thus some coins attributed to the Sassanians (from Iran during the 2nd to the 6th centuries A.D.), have been determined to be modern fakes because they had insufficient levels of gold as an impurity (20). The artificer was unaware that current silver stocks are too pure.

Bread, Beer, and Wine

It has already been argued that chemical technology was applied to food in the form of cooking at a very early stage. The next significant development of food technology was domestication of plants and animals, a biological rather than a chemical process. The baking of bread can be considered a biochemical process, and its roots go back 10,000 years or more in Southwest Asia (21). Baking may even have preceded domestication of grains. Humans would have found that the processing of wild grains could provide a stable, nutritious material through treatment with yeast and heat. Selection of superior strains of grain over many generations then resulted in plant domestication and settled farming.

Like bread, beer is not a naturally occurring food but must be created by human processing. The specific grain barley (*Hordeum vulgare*, from the wild species *H. spontaneum*) was one of the earliest cultivars, along with wheat, and it is the only grain from which true beer

can be made. Early beer did not contain hops, but was the direct result of the fermentation of barley. Both bread and beer were staple materials in ancient Mesopotamia and Egypt and probably required the development of pottery before they could achieve widespread use. A rice beer was consumed in China during their Neolithic period, 7000-5000 B.C. (22).

McGovern has tracked the production of wine back into Neolithic times (23). There is clear evidence for wine at the Iranian site of Hajji Firuz Tepe dating to 5400-5000 B.C., and even possibly earlier in transcaucasian Georgia. These studies are carried out by extracting residues from the interior of carefully excavated pots. The molecular marker that identifies exposure of the pot to wine is tartaric acid. Similar experiments for beer use calcium oxalate as the marker. The presence of starch molecules can indicate either bread or beer. Without chemical analysis, the archaeologist would have nothing more than a piece of pottery and no knowledge of its original contents. Thus ancient biochemistry enabled the alteration of natural foods to processed foods, and modern chemistry reveals the presence of these materials in the archaeological record.

Glass

Although sand and quartz are abundant sources of silica (a polymeric form of silicate with the overall formula of SiO_2), its melting point at ca. 1700ºC is far too high to have been achieved by ancient craftsmen. Nonetheless, silica (usually from quartz) is the principal component, or former, of glass. Numerous beads, called Egyptian faience, were produced during the third and fourth millennia B.C., but they involved sintering rather than melting of quartz. Complete melting, however, was required before practical objects such as vessels could be produced. Some time around 2000 B.C. in Egypt or Mesopotamia, it was discovered that the melting point of silica could be lowered significantly by the addition of a second material, or flux. The technology could have emerged from either a pottery or a metallurgy tradition, as both had procedures that could be considered precursors of glass. Around 1500 B.C., glass manufacture suddenly appeared as a major industry in Egypt. The Egyptians, and possibly their Mesopotamian predecessors, used soda ash (sodium carbonate) as the flux from both inorganic sources such as the mineral natron and organic sources such as alkali plants (salcornia). A third component was added as a stabilizer to counter the high solubility of sodium that would destabilize the product. It contained less soluble ions such as calcium or mag-

nesium from sources such as lime. The resulting product for millennia has thus been called soda lime glass. Basically the same formula has been used up to the present in inexpensive window glass.

Most silica sources contain iron ions as an impurity, conveying a light blue-green color to the glass. This color is visible to the eye by viewing a glass pane from its edge. The normal view of glass is through a width of less than an eighth of an inch. Viewing a glass pane from the edge gives a depth of six inches or a foot or more, and suddenly the glass appears to be greenish. The color of the iron ions is manifested by their greater numbers in the greater depth. Ancient chemists realized that adding antimony (which of course they did not know as antimony) to the glass raw material counteracted the coloring properties of iron (which they also did not know as such). The antimony served to oxidize the more colored Fe(II) to the less colored Fe(III), decreasing the coloring. High antimony glass was in use from the sixth century B.C. to the fourth century A.D. Chemical analysis of glass for antimony thus can indicate the general period of production. In Roman glass, manganese replaced antimony as the decolorant. Wherever Roman influence was uppermost, the level of antimony decreased and that of manganese increased, another chemical fingerprint for glass technology.

Mediterranean glass technology developed in many directions. Various elements could make it colored: deep green from copper, red from copper in a different oxidation state, violet from iron and manganese, blue from cobalt, turquoise blue from copper and iron, and yellow from lead and antimony, usually at levels under 1% as the oxide. Normally such glass was transparent, but the addition of sufficient lead (giving a yellow color), antimony, or tin (giving a white color) made the glass opaque. The Egyptians learned how to bond glass to metal, resulting in the technology of enameling. A Hellenistic innovation was layered or cased glass, by which several glass layers were placed one on top of the next, and designs were cut through to different layers, creating cameos. Dichroic glass, which exhibits one color to reflected light and a different color to transmitted light, appeared in the late Roman Empire. The Lycurgus Cup, dated to the fourth century A.D., contains nanometer-sized particles of gold and silver, whose dimensions are appropriate to reflect or transmit light of different wave lengths. Nanotechnology also was known to the Chinese, who employed nanodimensional gold particles to produce brilliant red colors of the porcelains termed *famille rose*.

Sayre and Smith first recognized the importance of bulk elemental composition on the properties of glass (24). The roles of sodium as a flux and of antimony or manganese as a decolorant have been mentioned. Lead was used as an alternative to sodium as the flux in Mesopotamia and China and as a means to enhance the brightness of the glass by the Romans and later by Islamic and European cultures. Early Chinese glass contained barium as well as lead as the flux, but the more stable soda glass, introduced by diffusion from the West, replaced the earlier formulation after the Eastern Han Dynasty (220 A.D.). After the fall of the Roman Empire, sources of soda become unavailable to glass manufacturers in Europe away from the Mediterranean coast. Plant ash rich in potassium was used as the flux instead. As a result, medieval glass from much of Europe was high in potassium.

The elemental composition of glass provides an amazing witness of the ebb and flow of economic, environmental, and social pressures. Antimony was a better decolorant than manganese, but the Romans preferred the latter, probably because of its availability. China developed lead and barium fluxes independently of Western discoveries but quickly adopted the superior soda formulation when it become known to them. Medieval Europe moved away from soda glass in favor of potash glass for reasons of availability. Lead was found to clarify glass to a point of sheer brilliancy. Small particles of gold could deliver very unusual appearances. Almost any color could be achieved with the right additives. These discoveries must have been the result of careful observations and luck, just like most of science.

Rubber

Technological developments in the Western Hemisphere generally occurred much later than those in the Old World. Thus pottery did not appear until about 2500 B.C. and metallurgy some time before 250 B.C. The chemists of the New World, although working later in time, were no less innovative than those of Southwest and East Asia. For example, they created a blue pigment used on wall murals that was a combination of the vegetable dye indigo and a specific white clay called attapulgite, making what today would be called an organic-inorganic hybrid. This material has proved to be very stable to acid, base, solvents, light, normal heat, and biological corrosion, allowing the mural colors in Bonampak, Chiapas, to remain bright for hundreds of years in the jungle.

In addition, Mesoamerican chemists created processed rubber about 4000 years ago. It was an easy step to recognize the useful properties of the sticky exudate of the tree *Castilla elastica*. The polymer is polyisoprene, identical to modern crude rubber from the South American plant *Hevea brasiliensis*. This latter species is preferred today because it can yield its exudate without killing the plant. *Castilla elastica* was widely available in Mesoamerica. When dry, however, the unprocessed exudate becomes brittle and loses its rubbery properties. Observations by Spaniards at the time of the Conquest indicated that the local chemists mixed the crude exudate with the juice from the morning glory vine, *Ipomoea alba*. A recent study of the nuclear magnetic resonance (NMR) spectra of ancient Mesoamerican rubber indicated that it is identical to modern processed rubber (25). It differed from the NMR spectra of the crude latex in the absence of proteinaceous resonances. The morning glory juice served not only to purify the exudate but also to generate cross linking, analogous to the modern process of vulcanization. The purified, cross-linked material retains its elastic properties.

The Mesoamericans used rubber primarily to make the ball for the religious activity termed *pelote*, now referred to as a ball game. *Pelote* courts are found at archaeological sites from the southwestern U.S. to Central America, indicating an extremely widespread activity, which has been associated with agricultural fertility. In addition, rubber was occasionally used for bands to hold implements to handles and for decoration. These artifacts have been excavated particularly from the *cenotes* or water-filled sinkholes in Yucatan. Without chemical processing, the rich ceremonial culture of the *pelote* game would never have developed. Western civilization did not have vulcanized rubber until the nineteenth century.

Overview

Hundreds of thousands of years ago, hominids from a species ancestral to *Homo sapiens* became chemists by learning how to control fire. This control provided heat, light, and protection, aiding hominids to expand throughout this tenuous and dangerous world. Fire later provided the means to process food, through cooking, into more stable, safer materials and to process flint and other stones, through annealing, into more useful materials. By mixing minerals with natural tars, humans created a new material (asphalt) with superior properties for adhesive purposes. Fire also enabled humans to convert

limestone and gypsum into a powder. Addition of water formed a slurry, which could be formed into structures and allowed to harden into shaped stone. All these chemical processes were in use more than 10,000 years ago.

Chemistry and biology worked together to give rise to the Neolithic revolution, as hunters and gatherers became farmers and began to congregate in villages. Chemistry's first profound contribution to this revolution was pottery, which appeared in Japan about 14,000 B.C., Turkey 8500 B.C., and the New World 2500 B.C., all most likely independent discoveries. Ceramic figurines existed much earlier, but the invention of utilitarian ceramic vessels provided rich uses in early Neolithic cultures. The earliest system of writing, cuneiform, invented by the Sumerians about 3200-3000 B.C., was executed on baked clay. Thus chemistry provided a key element in the development of that most basic characteristic of civilization, writing. The Sumerians appreciated how momentous their invention was and celebrated it in one of their later epics:

> Before that time writing on clay had not yet existed,
> But now, as the sun rose, so it was! The king of
> Kullaba had set words on a tablet, so it was!

Kullaba was ancient Uruk (the exclamation points have been provided by modern editors).

With the availability of ceramic vessels, processed food could be stored and manipulated. Grain was converted to bread and beer, grapes to wine. The baking of bread was carried out by 8000 B.C. In fact, the sequence of events is not clear, as to whether grain domestication (a biological process) or baking of bread (a biochemical process) came first. The invention of beer provided a staple drink that may have been safer and more nutritious than water sources subject to microbial contamination (many microorganisms cannot exist in the presence of ethanol).

Humans moved from the Stone Age (which includes the Neolithic) to the various ages of metals (Chalcolithic, Bronze, Iron) by means of a series of chemical discoveries. The mixing of elemental materials into alloys improved the properties of copper (as bronze) and of iron (as steel). The smelting of ores allowed natural oxides and sulfides to be converted to the elemental form needed for metallic materials. Stone tools and weapons were replaced with metallic ones.

The invention of glass was made possible by the chemical discovery that a mixture of sand with soda

could be liquefied and converted to useful objects on solidification. Less revolutionary than metals (the times were referred to as the Bronze Age, not the Glass Age), glass nonetheless allowed both utilitarian objects and materials appreciated just for their beauty to be created on a scale heretofore unknown.

All these chemical discoveries, except possibly glass, were made by preliterate societies; yet they helped define human culture wherever it was found.

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GRANVILLE PERKINS AND LEPROSY CHEMOTHERAPY IN THE PHILIPPINES

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Introduction

This article examines the career of Granville A. Perkins (1891-1985), an American organic chemist who made significant contributions to the chemical fight against leprosy in the Philippines, before returning to America to take up a career in chemical industry. Perkins also pursued research in theoretical chemistry and quantum mechanics. He came to my attention in a footnote in Russell's seminal history of the concept of valency, where the text reads (1):

> In both Lewis and Langmuir appear formulae with shared pairs that must have originated from one and the same atom, *e.g.*, in the ions of the oxy acids. Attention was drawn to this "borrowing union" by Perkins; it was termed a "semi-polar bond" by Sugden *et al.*, and a "co-ordinate link" by Sidgwick, …

The names of Lewis, Langmuir, Sugden, and Sidgwick will be familiar to anyone who has taken an interest in the twentieth century history of chemistry, but the question arises, 'who was Perkins?', since this appears to be his only contribution to the development of the valency concept and he is not remembered for other contributions to the chemical literature. In the work referred to by Russell, Perkins suggested that the coordinate bond be represented by the symbol ω, but this was not adopted. Chemists clearly preferred Sidgwick's arrow.

The Perkins paper to which Russell refers was published in the *Philippine Journal of Science* (2).   This article was not the first public expression of Perkins' interest in theoretical physics and chemistry, since it had been preceded by one on the electron (3); and it was succeeded by three others, one on relativity (4), one on double bond additions (5), and one on molecular structure (6).   Many years later, after he had retired from employment in the American chemical industry, Perkins returned to this interest and published a number of papers in the field of quantum mechanics that will be referred to later in this account.

Perkins' Career

Granville Akers Perkins was born in 1891 in Lin Ching, China, where his American parents were Congregational medical missionaries, his mother (née Estrella) being one of the early women medical graduates. The family returned to the United States around the turn of the century, and Perkins' baccalaureate degree was awarded by Cornell University (A.B. 1913), following which he taught at the Institute of Chemistry of the University of Puerto Rico (1913-1915). While there, he met and married Marie Waring, who was teaching in an American school there; their first daughter was born in San Juan. Perkins then spent a short time as a junior chemist in the U.S. Department of Agriculture before taking up an instructorship in chemistry at the University of Pittsburgh, from which institution he was awarded the Ph.D. degree in 1915. After a brief appointment with E. I. Du Pont de Nemours in 1917, he spent the war years as a Lieutenant in the U.S. Army Chemical Warfare Service. After World War I came the phase of his career that receives most attention in this article, for Perkins took up

an appointment in the Bureau of Science of the Philippine Islands, in Manila. Following some involvement with preparation of materials for leprosy chemotherapy, he transferred in 1922 to become Chief Chemist at the leper colony on the Philipines' Culion Island, where he remained until 1927 (7).

Upon his return to America, Perkins first worked as a research chemist at the American Meat Institute Foundation in Chicago (8); but finding the climate there too different from what he had obviously enjoyed in Puerto Rico and the Philippines, he moved after two years to South Charleston, West Virginia, to undertake research in organic chemistry for the Carbide and Carbon Chemical Company, a division of Union Carbide. There a second daughter was born, and Perkins' career progressed as he became assistant director (1931-1944) and then director of research (1944-1951). Among his early work with Carbide was involvement in the development of the plastic Vinylite, a copolymer of vinyl chloride and vinyl acetate. During the years of World War II he was deferred from military service because of his work on synthetic rubbers involving butadiene, but was pleased to see his elder daughter taken into the U.S. Army as a physical therapist.

Briefly to recount the later years of his industry career, in 1951 Perkins became Vice President in the company's Carbide and Carbon Division, requiring a move to Mamaroneck, NY, where the family lived until he retired in 1956. In the mid-1960s, he and his wife then moved to Florida where he died over two decades later at age 94.

Paul Freer and Government Science in the Philippines

The Philippine Islands had long been a Spanish colony; but as the end of the nineteenth century approached, change was in the wind. There were repeated rebellions by indigenous groups during the 1890s, and these were to some extent (as in Cuba) supported by the United States. Although peace was established between the rebels and their colonial overlords in 1897, within a year the Spanish-American War had broken out, and under the Treaty of Paris that formalized its ending, the islands were ceded to the United States. Although the annexation was opposed by some in America, and certainly by many in the Philippines, the United States replaced Spain as the colonial power and within a year or two had reached agreement with the rebel groups who declared their new allegiance in April, 1901. Their

struggle continued through more peaceful means over the next few decades, with Manuel L. Quezon, President of the Senate, leading repeated delegations to the United States in the 1920s seeking independence. It was finally achieved in 1946, after World War II delayed the fulfillment of President Roosevelt's promise of 1934 that it would come within ten years.

The U.S. administration moved quickly after the end of the Spanish American war to establish civil government in the Philippines, one of the initial appointees being Dean C. Worcester, a zoology professor from the University of Michigan who became Secretary of the Interior (9). In 1901 the administration founded the Bureau of Government Laboratories, and Worcester recruited his Michigan colleague, Paul Caspar Freer (1862-1912), to head it (10). Freer was a medical graduate and organic chemist with a substantial record of published research, who had taken his M.D. degree at Chicago, earned his Ph.D. degree in 1887 in Munich under von Baeyer, and also worked for a year as assistant to W. H. Perkin in Manchester. He was granted leave from his Michigan position for three years to join Worcester in the Pacific, but eventually resigned and became a permanent employee of the Philippine government.

The Government Laboratories in Manila were set up with multiple aims: to research the resources of the Philippines, to work on tropical diseases, and to provide services to government agencies responsible for customs, mining, forestry, agriculture, and health. Members of the scientific staff of the Bureau were recruited (at generous salaries) from the United States and all except directors were employed under the Civil Service Commission at Washington. Guest workers were also welcome (11). Two years after its foundation, Freer was able to report the near-completion of a laboratory and the arrival of the first staff members for branches of chemistry, bacteriology, pathology, botany, entomology, and serum production (12). Of particular note was the list of 15 reports covering botany, infectious disease, and chemistry, the latter including one on gutta percha and rubber in the Philippines (by Dr Penoyer L. Sherman) and one by Freer himself on the preparation of benzoyl acetyl peroxide and its use as an intestinal antiseptic in cholera and dysentery.

In 1905, following his resignation from the University of Michigan, Freer was designated Director of the Bureau of Science. In this position, held until his death, he argued successfully for the foundation of a medical school, which opened in 1907 with Freer as

foundation Dean. Two years later the school was merged with the newly formed University of the Philippines, when Freer was also appointed to a chair of chemistry (13).

A lasting monument to Freer's work was the *Philippine Journal of Science*, which he founded a few years after taking up his appointment, in order to provide a vehicle for publication of his colleague's results. He made it a journal that would meet his exacting standards, and as editor he kept a firm hand on the nature and quality of the work published there. There was a direct correlation, of course, with the quality of men that Freer attracted to positions in Manila, and one example serves to highlight this. It is the presence on the staff of one Gilbert N. Lewis (1875-1946), who spent the year 1904 as Superintendent of Weights and Measures in the Bureau, between his appointments at Harvard and then MIT, before he moved to Berkeley where the major part of his career was spent. Like Einstein at about the same time but half a world away, Lewis did not find that his public service duties hindered his ability to contribute to science at the very highest level. Servos, in covering the history of this period notes that (14):

> While in Manila, Lewis experimentally determined the free energy of formation of water from its elements and became intrigued by the experimental challenges posed by such determinations.

In order to calculate the electrolytic potential of oxygen by an indirect method, Lewis needed to know the decomposition pressure of silver oxide at 25°, and this he determined by extrapolation from pressures measured at higher temperatures. His result, 4.9×10^{-4} atmospheres was reported in a Bulletin of the Laboratory (No. 30) and also in the local journal (15).

While the *Journal* carried many articles about natural resources of the Philippines, including their chemistry, the chemists also published the results of what today we would call 'curiosity led' research that continued the interests they had developed before coming to the Philippines. Three important contributors were H. D. Gibbs (1872-1934), H. C. Brill (1881-1968), and D. S. Pratt (1885-1920) (16), physical organic chemists who in the years 1913-1916 published on absorption spectra, rates of hydrolysis of esters, and the photochemistry of methanol. Harry Drake Gibbs (Ph.D. Stanford University) spent the period 1907-1914 in the Bureau, for the last three years of which he was also Associate Professor of Chemistry at the University of the Philippines. His subsequent career included periods in the U.S. Department of Agriculture and the U.S. Public

Health Service (17), but in between these he was a research chemist with the Du Pont company where he discovered the vanadium oxide-catalyzed vapor-phase air oxidation of naphthalene to phthalic anhydride (18). Harvey Clayton Brill, another Michigan graduate (Ph.D. in organic chemistry, 1911), served in the Philippines during 1913-1916 while on leave from his *alma mater*, Miami University in Oxford, Ohio, to which he returned to continue a long career in teaching and research (19). Brill achieved emeritus status at age 71 in 1952 but remained active for many years and was accorded the honor, by the American Chemical Society, of being chemist of the year for the Cincinnati Section in 1959.

The careers of Lewis, Gibbs, Brill, and no doubt others who spent some of their early career years in the Philippines further testify to the quality of staff recruited by Worcester and Freer. None of the chemists stayed for long, perhaps seeing a stint in the Philippines as a contribution to international development, since their later careers developed in directions other than those they had pursued in Manila. Perkins, while he was in the Bureau Laboratory, would presumably have done his share of routine analytical work, but like Lewis (although without the latter's impact) he also conducted research on chemical physics in his own time.

The chemical impetus given to the new institution by Freer survived his early death in 1912, at age 50, which was noted in the *Journal of the American Association for the Advancement of Science* (20). The AAAS also published the resolution expressing admiration and regret, drawn up by his colleagues in Manila (21). This resolution also headed a supplement to the July, 1912 issue of the *Philippine Journal of Science*, which carried a number of articles concerning Freer's life and work, as chemist and administrator.

Leprosy Chemotherapy and Ghaulmoogra

In the days before effective chemotherapy for leprosy, it was common to isolate infected people from society in leprosaria, from which few returned (22). It is little wonder that the Philippine establishment at Culion (discussed below) attracted the epithet 'island of the dead.' Although many substances including arsenic were touted as treatments for leprosy, the only medication available to infected persons that seemed to do any good was chaulmoogra oil, derived from the seeds of a tree of the *Hydnocarpus* genus. Administered orally it produced nausea as a side effect, and by injection it caused considerable irritation. Variants on the chaulmoogra theme

were explored without notable success by a number of groups, including the scientists and doctors in the Philippines; but it was not until the advent of diphenyl sulfones in the early 1940s that effective chemotherapy became available (23).

The use of chaulmoogra oil is believed to have originated in Burmese medicine some centuries ago, and to have been carried into Indian, Chinese, and other south- and east-Asian cultures. As the twentieth century wore on, it became clear that, although showing *in vitro* activity, neither the oil nor its derivatives (see below) were the hoped-for specific cure for leprosy (infection with *Mycobacterium leprae*), but the thought that it might have certain more general therapeutic properties has maintained it as a material for continued study (24). It is difficult to find definitive evidence, but a recent judgment was that (25):

> Chaulmoogra oil seems to have made a significant contribution to the management of leprosy for many years, giving some hope where there had been none.

The principal ingredients of chaulmoogra oil are the glycerides of chaulmoogric and hydnocarpic acids. The molecular formulas and tentative molecular structures for these acids were established early in the twentieth century (26). Chaulmoogric acid, $C_{18}H_{32}O_2$, an isomer of linoleic acid, contains only one double bond (linoleic having two) and is moreover optically active (signifying the presence of molecular dissymmetry). Barrowcliff and Power postulated that its structure must contain a ring, and they formulated it with a cyclopentene or cyclohexene ring incorporated into a long paraffinic chain. Hydnocarpic acid is a homolog with similar core structure but with three fewer carbons in the chain and was regarded as less active pharmacologically.

The correctness of one of these proposed structures was proven by Shriner and Adams (27); Noller and Adams also completed syntheses of the achiral dihydro acids in 1926 (28). In that and the following year, Perkins

Granville Perkins in middle age when he was a research director with Union Carbide (photograph kindly provided by Perkins' daughter, Mrs. Barbara P. Clark)
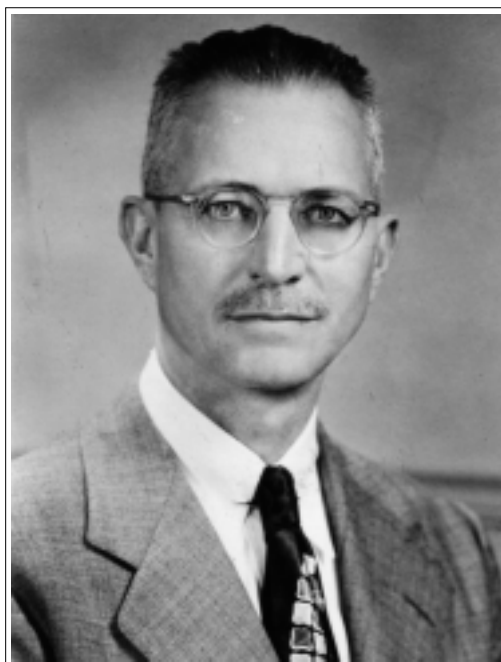
published the results of his research in the Philippines that culminated in a synthesis of the racemic mixture of the isomers of chaulmoogric acid (29). Synthesis of the fully optically active acid, involving the resolution of an intermediate with brucine, was achieved many years later (30).

Some applications of the oil in the early part of the twentieth century included its co-administration with adjuvants such as camphorated oil or creosote, while others relied on derivatization to yield mixtures of sodium salts or ethyl esters. The latter product, known as Antileprol and marketed by the Bayer Company, was claimed in the years before World War I to be effective against leprosy (31), and Granville Perkins was involved with it and similar esters in the Philippines where extensive investigations into their efficacy were conducted.

Perkins and the Culion Leper Colony

The welfare of sufferers from leprosy in the Philippines under the Spanish regime and in the early years of American administration was in the hands of Catholic priests of the Franciscan Order, but no medical care was provided apart from basic hygiene. Following an executive order by the Philippines administration in 1904, it was decided to establish a leprosy colony (later Sanitarium) on Culion Island, approximately 350 km SSE of Manila. The first group of 370 patients arrived in May 1906, to be cared for by the medical officer in charge of the colony, assisted by a Jesuit Father and four Sisters of St. Paul de Chartres, who acted as nurses (32).

Over the next fifty years, the colony was home to approximately 30,000 people, some 3,000 of whom were born there. The population grew steadily to a peak of 7,000 in 1935, but thereafter declined under the influence of three factors: many patients were declared 'negative' following treatment with chaulmoogra ester; the advent of sulfone medication offered real cures; and government restrictions on sufferers' living in the com-

munity were relaxed. (Until then sufferers were banished to leprosaria.)

A driving force in the administration of the Colony was Herbert Windsor Wade (1886-1968), an American scientist who earned an M.D. from Tulane University in 1912 (33). After working for several years in New Orleans, Wade married and he and his bride moved to Manila, where he had been appointed pathologist and bacteriologist in the Bureau of Science. He served in that position 1916-1918 and then as professor of pathology and bacteriology at the University of the Philippines, before joining the Culion Leper Colony as chief pathologist in 1922. In that year Granville Perkins also transferred from the Bureau to Culion, and together they launched a chemical assault on *Mycobacterium leprae*. Although Wade remained in Manila, he was appointed in 1931 medical director of the Washington-based Leonard Wood Memorial for the Eradication of Leprosy. Wood (1860-1927), a U.S. Army officer who was governor of Moro Province in the Philippines in 1903-1910, took a great interest in the development of the country under American administration.   After a stint in Washington as Chief of Staff of the U.S. Army, Wood returned to the islands as governor from 1921to1927 (34). Wade spent more than 20 years in the Philippines and was interned there in 1941-1945 when Japanese forces occupied the islands. Early in his directorship Wade founded the *International Journal of Leprosy*, which he edited almost until the time of his death. He had long served as a consultant to Culion. Upon his resignation from the Leonard Wood Memorial in 1948, he rejoined the Colony as pathologist and associate medical director until 1959, when he accepted the status of Pathologist Emeritus (35).

It is reported that Dr. Eliodoro Mercado (1866-1933) pioneered parenteral (that is, not by ingestion) treatment of leprosy patients with chaulmoogra oil at the San Lazaro Hospital, where he became a specialist leprologist (36). He presented the results of his work at the Second Regional Assembly of Physicians and Pharmacists of the Philippines, in Manila in 1914, but he seems to have had no connection with the chemists at the Bureau or the staff at Culion. The first evidence of work being undertaken on chaulmoogra in the government laboratories comes from two of Brill's papers (37), in the second of which the authors noted the lack of effect obtained with commercial Antileprol or the crude chaulmoogra oil itself and expressed surprise that this should be the case. The experiments, involving several batches of oil from different sources, were carried out

at the Culion Colony. A subsequent issue of the journal carried an article by the Chief of the Culion Leper Colony, illustrated with photographs to show the different types of external lesions found in the patients there (38).

Perkins was involved in the investigation of chaulmoogra even before he left the Bureau of Science in Manila (39), and that probably explains why he was chosen (or chose) to transfer to the Culion Colony. He began his first publication on chaulmoogra by recounting the history of its use. He noted that oral or external administration was giving way to intramuscular and intravenous injection, and that the efficacy of the sodium salts of the acids pointed to the acid structures, rather than those of the glycerides or associated impurities such as glycosides, as the therapeutic units. In his paper Perkins refers to Mercado and his work at the San Lazaro Hospital and offers some support for the theory of action advanced by Rogers (40), and also acknowledges Power's work with ethyl esters of the acids and the existence of subsequent patent coverage. Mercado was most successful with intramuscular injection of a mixture of chaulmoogra oil, camphorated oil, resorcine (the antiseptic phenol resorcinol) and ether (41). Irritation persisted when crude chaulmoogra oil was used, but this was found to be due to the presence of free acids in the oil, which could be removed by a purification process. Perkins also experimented with the mixed ethyl esters formed from chaulmoogra oil by transesterification with ethyl alcohol, and found that concentrated sulfuric acid was a superior catalyst to the dry HCl that had been used by earlier experimenters. His paper provides detailed instructions for the preparation of this ester in quantities up to 50 liters and its purification by distillation at reduced pressure. Some 200 liters were produced each month in Manila for use in intramuscular therapy at Culion. Following earlier work that had shown promise, the ester was injected together with 2% iodine, and clinical trials were also conducted with the 'soaps'— sodium salts of the chaulmoogra acids—that Rogers had pioneered. Perkins also noted Walker's theory that the acid-fast bacilli incorporate the unsaturated chaulmoogric acids into their 'fatty capsules' (cell walls), with fatal consequences, but that this property was not possessed by other unsaturated acids such as those of cod-liver oil (42).

Walker and Sweeney's work was followed up by one by Perkins' colleagues Otto Schöbl, of the Serum Laboratory at the Bureau of Science, who conducted *in vitro* trials of Perkins' materials with the acid-fast or-

A 1996 photograph of the laboratory at Culion, where Perkins worked in the 1920s. The bronze plaque at the entrance commemorates the work of H. W. Wade (photograph kindly provided by Mr. Harold Nou of Culion, whose mother was the Perkins' babysitter)

ganism *Bacillus tuberculosis* (43). Growth was inhibited on a two- to four-week time scale by

- chaulmoogra oil from India or Japan, but not by cod-liver or olive oil

- the oils of various closely related species, but not G*ynocardia odorata*

- sodium gynocardate but only to a minor degree by sodium chaulmoograte.

In a subsequent paper, Schöbl reported *in vitro* experiments with *Bacillus tuberculosis* and *Bacillus typhosus* and the acid-fast bacteria *Vibrio Choleræ* and a *Staphylococcus sp* (44). Only the chaulmoogra-derived substances suppressed growth of *B. tuberculosis*, and no other combinations produced suppression of any species except some essential oils, which were known to possess antiseptic properties.

Perkins' next paper summarized the physical properties and the chemical compositions of chaulmoogra and related oils from the literature and added extensively to the data collection as the result of his own experimental work (45). A subsequent paper giving practical details for the preparation referred back to this data compilation as 'Part I' and reported that oil of *Hydnocarpus wightiana* was the preferred source for obtaining the free acid (46). Perkins concluded his series of practical pa-

pers, revealing his command of experimental chemistry undertaken under what must have been difficult circumstances at Culion, with detailed instructions for the preparation of a number of esters of the mixed acids from chaulmoogra oil (47). Perkins acknowledged H. W. Wade's suggestions concerning these esters, each of which was prepared by transesterification of the oil with the appropriate alcohol, and the paper includes reaction curves showing yields of various mixtures that were stirred with sulfuric acid for up to 60 days at room temperature. Equilibrium was, however, reached more rapidly by boiling the mixtures. Each ester was purified by steam distillation and characterized by refractive index, specific gravity, acidity, and optical rotation.

Perkins' contribution to the work at Culion was vital to the attack on leprosy being undertaken there by Wade and his medical staff. As chemist, Perkins was responsible for characterizing the oils and related materials and producing large quantities of designated substances. With the encouragement of his superiors—all of his papers were published with the permission of the Director of Health and the approval of the Philippine Leprosy Research Board—he published detailed experimental methods and physical and chemical data on his products that would enable other researchers to follow in his footsteps. With this phase of the work complete and with a growing family, Perkins was anxious to de-

velop his career further. In 1927 he returned to the United States to take up a position in chemical industry. In his early years there, he continued in the laboratory but later moved into management.

Quantum Mechanics

Reference has already been made to several theoretical articles published by Perkins while he was in the Philippines, but later publications show that he retained his interest in this field and after a long break resumed active interest in it after his retirement from Union Carbide. While this is remarkable in itself—quantum mechanics being an unlikely hobby even for a trained scientist—he continued to publish until he was well into his tenth decade. His papers contain few references to original literature later than the 1930s, however. In the first of these papers he gave his New York address and acknowledged that part of the work "was completed while the author was associated with Union Carbide Corporation" (48), revealing that even while in senior management he was still 'moonlighting;' but thereafter his addresses were in Florida and no institutional affiliation was given (49). A candid assessment is that these papers reported sound but not groundbreaking work, which was seldom cited by contemporary authors. They represented a 'tidying up' of matters that had remained unresolved while the main field of research moved on.

Conclusion

Granville Perkins was one of a number of young American scientists who worked in the Philippines in the first few decades of the twentieth century before returning to the United States to continue their careers along more traditional paths in industry and academe. A number of them became well known during those times, but by-and-large their contributions to the development of science, and particularly chemistry, in the service of the Philippine government have been lost to sight.

Perkins' contributions were unique, because his chemistry underpinned a serious assault on leprosy that was devised and carried out on that remote Culion Island. His detailed recipes for the assessment and purification of raw materials, and for the preparation of derivatives of the natural products that make up chaulmoogra oil, added substantially to the repertoire available to other researchers who followed the fruitless trail of a leprosy cure through administration of chaulmoogra and chaulmoogra-derived materials. Subsequent drug discovery and application of the sulfones has changed the face of leprosy chemotherapy, leaving only a few experimenters to continue the exploration of the properties of the unusual fatty acids contained in that ancient remedy.

Alongside his contributions to leprosy chemotherapy and later the polymer industry, Perkins applied his chemistry to university teaching, to agriculture, meat science, and to war materials. His interest in quantum mechanics and chemical physics resides uncomfortably and unexpectedly alongside this working life in organic chemistry, but it was a personal interest that spanned 60 years of publishing and would have to be rated as something more than a hobby.

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Future ACS Meetings

March 13-17, **2005**—San Diego, CA

August 28-September 1, **2005**—Washington, DC

March 26-30, **2006**—Atlanta, GA

September 10-14, **2006**—San Francisco, CA

March 25-29, **2007**—Chicago, IL

August 19-23, **2007**—Boston, MA

April 6-10, **2008**—San Antonio, TX

August 17-22, **2008**—Philadelphia, PA

March 22-26, **2009**—Salt Lake City, UT

August 16-21, **2009**—Washington, DC

March 21-26, **2010**—San Francisco, CA

August 22-27, **2010**—Boston, MA

March 27-31, **2011**—Anaheim, CA

August 28-September 1, **2011**—Chicago, IL

March 25-29, **2012**—San Diego, CA

August 19-23, **2012**—New York, NY

KARL ELBS, 1858-1933

E. J. Behrman, Department of Biochemistry, The Ohio State University

Let fame, that all hunt after in their lives,
Live register'd upon our brazen tombs
And then grace us in the disgrace of death;
When, spite of cormorant devouring Time,
Th' endeavour of this present breath may buy
That honour which shall bate his scythe's keen edge
And make us heirs of all eternity.
Shakespeare, *Love's Labour's Lost*, I, i, 1

A chemist's labors are not lost (at least if he follows Faraday's second and third instructions) (1), but they are often not remembered or, if so, not properly attributed. It has been argued that scientific work should be published anonymously as it is the work that matters, not the name of the scientist. But there are many arguments against this both from the point of view of human nature (see epigraph) and also because of the importance of making links in the history of science.

Karl Elbs was not in the first-rank of chemists of all time, but he was among those at the top of his profession in his own time. How has his memory survived? Elbs' life illustrates the point that sometimes what one supposes to be one's best achievements are not in fact those that endure.

A brief curriculum vitae follows: 1858, born, Alt-Breisach/Baden; 1880, D. Phil., Univ. Freiburg; 1883, Habilitation, Univ. Freiburg. 1887; Ausserordentlicher Professor, Univ. Freiburg. 1894; Ordentlicher Professor and Direktor des physikalisch-chemischen Laboratoriums, Univ. Giessen. 1913; Professor der Leitung des chemischen Laboratoriums, Univ. Giessen. 1929; retired. 1933; died, Giessen. His mentor for his doctorate at the University of Freiburg was Adolph Claus (1838-1900), discoverer of phenazine and the author of two books on organic chemistry (1866 and 1871). Elbs' dissertation on derivatives of amarine resulted in two publications with Claus in 1880 and 1883. By 1887 he had published 19 papers and was appointed to a professorial post at Freiburg. In 1894 (9 papers and 2 books later), he moved to the University of Giessen (now Justus-Liebig-Universität Giessen) where he remained until his retirement in 1929.

Among Elbs' most famous colleagues were Franz Fischer (1877-1947), co-inventor of the Fischer-Tropsch synthesis of gasoline from coal, who worked with Elbs on the electrosynthesis of Pb(IV) compounds, and Otto Schönherr (1861-1926), who collaborated with Elbs on optimizing the electrosynthesis of peroxysulfates. He later moved to BASF to develop a practical method for the oxidative fixation of nitrogen (Luftverbrennung).

Elbs was best known in his own time as one of the founders of quantitative electrochemistry. Electrochemistry, discovered by Davy and Faraday, and brought into prominence by Kolbe, was developed as a quantitative science by Elbs, Gatterman, Löb, Tafel, and Haber. Elbs and his students studied the reduction of aromatic nitro compounds extensively, with particular attention to variation in voltage, current density, and electrode material. The reduction of ketones also received much attention. Other important areas of electrochemistry that were studied included the formation of peroxysulfates, the iodination of aromatics, the formation of Pb(IV) compounds, and the synthesis of iodoform. His work is still referenced in current organic electrochemistry textbooks. Brockman (2) cited Elbs' work on 81 pages out of 339. On page 2 he states (2):

But at the very end of the 19th century, the quantitative relations [of electrochemistry] were brought into prominence by Elbs, Haber, and others.

Glasstone and Hickling (3) likewise give many references to the work of Elbs, particularly in Chapter 5 on "Organic Reduction Processes" and in Chapter 7 on "The Polymerization of Anions." Fichter (4) published a valuable compilation of organic electrolytic reactions; Elbs' work is cited on 72 pages (out of 308). Later reviews of organic electrochemistry still contain many references to Elbs' work, although with decreasing frequency. Swann (5) and Allen (6) contain many such references. Finally, the gigantic (1,550 pp) 3rd edition (1990) of Lund and Baizer's *Organic Electrochemistry* (7) still retains six references to Elbs' papers on the reduction of nitrobenzene, azoxybenzene, and various ketones. (The 4th edition of this standard work lacks an author index.) Elbs' name does not appear so frequently in more general histories of chemistry. I have examined most of the relevant titles listed by Partington (1, pp xvii-xxi). Elbs is cited in only two (8, 9).

The other side of Elbs' fame lies in the fact that two organic reactions bear his name. (The 12th edition of the Merck Index lists 425 "Organic Name Reactions;" 57 chemists are associated with more than one. Emil Fischer wins first place with six). These are the Elbs Reaction and the Elbs Oxidation. Both merited chapters in *Organic Reactions* (10, 11). The Elbs Reaction is a cyclodehydration of *o*-methyl- or *o*-methylene-substituted diarylketones to yield anthracenes, while the Elbs Oxidation is the reaction of peroxydisulfate ions with phenolate ions to give (principally) the phenol *p*-sulfate. The Elbs Reaction was developed by Elbs between the years 1884 and 1890 from the original observations of Behr and van Dorp. The Elbs Oxidation dates from an 1893 paper in which *o*-nitrophenol was converted to nitrohydroquinone.

Another measure of how a scientist is remembered is through a search of the Online Science Citation Index. This index records citations in papers published since 1980. Elbs' papers are cited 52 times. The figure shows a plot of the numbers of papers (books are excluded) published by Elbs as a function of the year of publication. Superimposed on this is a plot of the number of times that papers published in a particular year were cited. Frequently cited papers and their subject matter are (in order of frequency): the synthesis of nitrohydroquinone, *J. Prakt. Chem.,* **1893**, *48*, 179-185 (19 times); oxidative coupling of two molecules of vanillin, *J. Prakt. Chem.*, **1916**, *93,* 1-9, 18 times); syntheses of 2-substituted benzo-1,2,3-triazoles, *J. Prakt. Chem.,* **1924**, *108*, 209-233 (17 times); benzotriazoles (the original paper), *J. Prakt. Chem.*, **1903**, *67*, 580-584 (12 times); homologs of anthracene, *J. Prakt. Chem.*, **1890**, *41*, 1-32 & 121-151 (6 times). The first and last are descriptions of what are now known as the Elbs Oxidation and the Elbs Reaction.
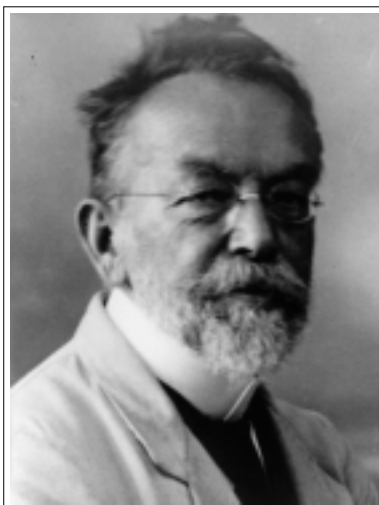
In addition to about 80 papers, Elbs was the author of one of the first compendia summarizing methods for the preparation of organic compounds (in two volumes), a small, very popular book on storage batteries (five editions), and a text book detailing laboratory methods for various electrolytic preparations. The latter was published in two German editions and also in French and English translation (see Appendix 1).

Karl Elbs

Appendix 2 lists the chief sources used for this historical account. Biographers Foerster and Brand both published papers with Elbs.

I end with a quote (in translation) from Brand's obituary.

> Elbs was a splendid and uncommonly energizing teacher whose lively lectures enthralled all of his listeners. He had the utterly amazing gift of describing even the most complex procedures in a simple and understandable manner. He took great care in the writing of formulas, which he wrote clearly and understandably on the board. When administrative and testing duties occupied less of his time, Elbs visited the laboratory, sometimes even twice per day, for the express purpose of helping his students. He discussed in detail the exercises on the board with them. Everyone who worked in Elbs' institute will fondly recall these energizing and profitable hours. Professor Elbs was an upright, genuinely patriotic man who openly expressed what he considered to be just and right without ever giving offense. His modest character never allowed him to step into the foreground and he did not look for outside honors.

A preliminary account of this paper has appeared (12).

Envoi

" Those ignorant of the historical development of science are not likely ever to understand fully the nature of science and scientific research. This can be said in support of the view that scientists should not restrict their studies entirely to the present edifice of knowledge." (13)

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I thank D. M. Behrman and M. Davis for translations, K. Omlor for diligent work collecting Elbs' papers, E.-M. Felschow, archivist at Justus-Liebig- Universität Giessen, for supplying the photograph, and Prof. V. Gopalan for the *envoi*.

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Appendix 1. Books by Karl Elbs

Die Synthetischen Darstellungsmethoden der Kohlenstoff-Verbindungen, J. A. Barth, Leipzig, Vol. 1, 1889, 294 pp; Vol. 2, 1891, 474 pp.

Die Akkumulatoren, Barth, Leipzig, 1st ed., 1893; 2nd ed., 1896; 3rd ed., 1901; 4th ed., 1908; 5th ed., 1919, 48 pp.

Übungsbeispiele für die Elektrolytische Darstellung chemischer Präparate, Knapp, Halle, 1st ed., 1902; 2nd ed., 1911. French translation by E. Leriche, Dunod, Paris, 1903; English translation by R. S. Hutton, Arnold, London, 1903, 99 pp.

Appendix 2. Chief Sources of the Biographical Material

A. G. Debus, Ed., *World Who's Who in Science from Antiquity to the Present*, Marquis, Chicago, IL, 1968, 517. This source lists a nonexistent book, *Die Anthrachinone*, 1900, evidently taken from the *Neue Deutsche Biographie*, **1959***, 4,* 436.

J. C. Poggendorff*, Biographisch-literarisches Handwörterbuch* , **1904***, 4*, 374; **1925***,5*, 333; **1936***, 6*, 652.

F. Foerster, *Z. Elektrochem.*, **1928***, 34*, 420a-420b (70th birthday).

E. Weitz, *Ber. Dtsch. Chem. Ges.*, **1933***, 66*, 74-75 (Obituary).

K. Brand, *Z. Elektrochem.*, **1933***, 39*, 923-926 (Obituary).

Other biographical details can be found in Hans Steil's extensive account of Elbs' career (Ref 14), which focuses on personal details and includes hitherto unpublished material. This account is part of a two-volume work celebrating 115 distinguished scholars from all fields who held positions at Universität Giessen in the first half of the 20th century. I am indebted to Prof. Joseph Fruton (Ref. 15) for this somewhat obscure reference, which I otherwise would have missed.

Publication and Citation Frequencies
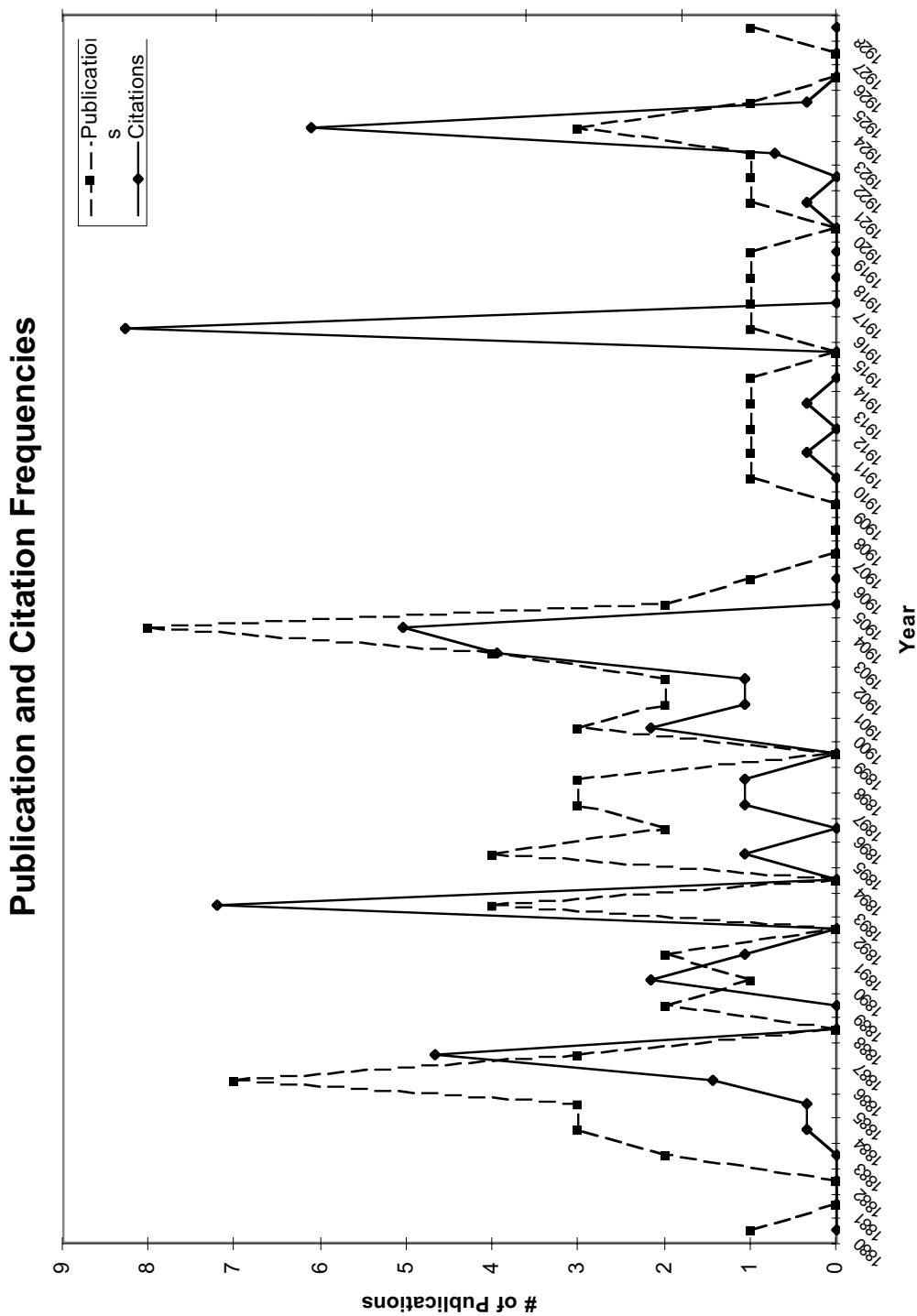
Legend for Figure 1:   The dotted line gives the number of Elbs' publications, excluding books, as a function of the year of publication. The solid line shows the number of times publications for a particular year were cited in the period 1980 to mid-2003, according to Science Citation Index.

THE HEART OF STEEL: A METALLURGICAL INTERPRETATION OF IRON IN HOMER

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The *Iliad* and the *Odyssey* co-evolved with the use of iron, and so a detailed examination of iron in the Homeric poems has the potential to flesh out a "fuller cultural history" (1) of the Greeks: what they considered the properties of iron objects, and how iron acquires these properties. I believe the texts distinguish three types of iron: bloom iron, wrought iron, and steel, despite the fact that most translations simply use the English word "iron" for all three, and thus render anemic both our appreciation for ancient Greek culture and the poetic richness of the texts themselves. This paper is an attempt to fortify both.

I hope this survey will contribute to the narrative of early chemistry, since the epics appear well after the earliest applications of chemical technologies, as revealed by archaeology and physical anthropology, and before theories of Hellenic, Indian, and Chinese philosophers of the first millennium B.C.E. (2, 3). According to the "composition-in-performance" model of epic transmission, the Homeric texts grew over a thousand-year period, from the time bards began singing tales of the Trojan Wars in the second millennium, when iron was an odd rarity and Greek writing unknown, to the standardization of written texts in the second century B.C.E., when iron was ubiquitous (4). Because the two epics flowered simultaneously, contemporary scholars do not attempt to fix either the *Iliad* or the *Odyssey* as prior in composition and feel free to use the texts to interpret each other (5, 6).

In this paper I summarize all references to iron in both the *Iliad* and the *Odyssey*, using the "iron heart" metaphor to illustrate that a fuller appreciation of the complexity and variety of references to iron is important on a poetic level, as well as historical (7). My method has depended heavily upon the Perseus Project, a digital library of ancient texts at Tufts University, where the *Iliad* and *Odyssey* appear in the original Greek and in several English translations. This library includes a searchable word frequency tool, which tells the reader how many times, in what form, and where in the original Greek text words with a particular root occur (8). In the discussion that follows, literary quotations are taken from Fagels' translations of the *Iliad* and *Odyssey* (9, 10), except where noted. Line references refer to the chapter and line where the term for iron appears in the original Greek texts, as displayed by the Perseus Project. For brevity, I assume a reader who is familiar with the plots of both epics.

As Hard as Iron

Most references to iron are just what the reader would expect. Many prosaic objects in the *Iliad* and *Odyssey* are made of iron (*sidêros* in Greek). These include weapons, like blades (Od. 19:13 and Il. 18:34), a club (Il. 7:136 and 142), and the axe heads of the suitor's contest in *Odyssey* 21. While not as glorious as arms made with bronze, gold, or silver, iron objects are tough and serviceable. Hera's war chariot may have wheels, railings, and yoke of glittering precious metals, but the axle, the

hidden part of the chariot that must bear her considerable weight, is iron (Il. 5:722). Athena boasts to Telemachus that Odysseus can scheme his way out of any impossible situation, even if he is chained in iron bonds (Od. 1:203). The massive gates of Tartarus are iron (Il. 8:13).

The poems invoke iron's familiar hardness to depict nonmetallic things. In the *Iliad*, the noise of war is an "iron din" (17:425) and Patroclus' funeral pyre burns with the "iron rage of fire" (23:177). In the *Odyssey,* Eumaios and later Odysseus observe that the infamy of the suitors spreads to the "iron skies" (15:328, 17:564), evoking images both of the sky as an inverted metal bowl and of the divine order as impervious to injustice.

People are juxtaposed with iron in interesting ways. In one instance, human flesh is explicitly *not* iron, for it cannot resist the cutting bronze (Il. 4:509). In several others, people, or their parts, are iron-like. The disguised Odysseus, upon seeing Penelope weep, keeps such composure that his fixed eyes are like iron (Od. 19:211). Similarly, the nurse Eurykleia describes herself as iron for her firm resolve (Od. 19:493). Finally, Odysseus (Od. 4:292), Penelope (Od. 23:172), Achilles (Il. 22:357), and Priam (Il. 24:205 and 608) all are described as having "iron hearts" beating in their chests. These references to iron are easily disregarded: iron hearts are strong. But not all forms of iron are equally hard. Some are soft or brittle, and this raises the novel possibility that iron in the texts is not always synonymous with toughness and impregnability.

Greek Warrior

Bloom and Wrought Iron

The Homeric poems refer to iron in ways that seem to differentiate bloom iron, wrought iron, and steel, and thus part of the poems' composition occurred when all three types of iron objects were in wide use. Ironworking likely originated from the process of smelting copper to make bronze (11, 12, 13). The techniques for making bronze appeared around 3200 B.C.E., and rely on the fact that copper melts at 1200° C, while iron melts only

above 1530° C. Copper ores were heated in a furnace, along with fluxing additives like hematite, an iron-containing ore that was needed to adhere to impurities. At the temperatures attained by charcoal furnaces, the copper melted and sank to the bottom of the furnace, while slag, the solid, iron-containing waste, floated on top.

After recovery of the molten copper, artisans made a bronze alloy suitable for casting by the addition of ~10% tin. The slag was discarded. At some time, someone discovered that the solid waste could be worked within a fire, rather than simply thrown away. Although archaeologists have found plenty of iron ornaments or their rusted relics from Bronze Age sites in the eastern Mediterranean and Southwest Asia, bronze artifacts are far more numerous (14, 15). The wealthy classes preferred bronze over iron because bronze could be easily cast and was hard enough to hold a cutting edge. Iron could only be worked in the solid form and was softer than bronze in its wrought form. Because bronze was so expensive and the potential utility of iron was unrealized, most common people relied on stone tools for ordinary use (16).

During the Bronze Age, iron appears to have been valued more as a curiosity than a commodity. During the reign of Hammurabi in Babylonia (c.1792–50 B.C.E.), iron was approximately thirty times more valuable than silver, and more than fifteen times more valuable than copper (7). The crude miniature headrest and wrought iron tools found in the tomb of Tutankhamen (c.1350 B.C.E.), show that the metal was valuable enough to place with the Pharaoh's funerary trove and rare enough that the Egyptian artisans were unaccustomed to working it (17). Tutankhamen's treasure also included an exquisite dagger with an iron blade, the only artifact of its kind discovered in a Bronze Age site (13).

The Mediterranean Iron Age starts in earnest about 1200 B.C.E., when trade routes for the copper and tin needed to make bronze were disrupted. Locally found iron ores (hematite, limonite, magnetite, and pyrite) were used to make inexpensive iron objects, and within a few centuries iron eclipsed bronze, stone, wood, and bone

for utilitarian purposes. The smelting of iron required little beyond the techniques required for bronze production. The iron ores were first heated in the reducing atmosphere of charcoal furnaces, which reached a maximum temperature of about 1200° C. Since iron does not melt below 1530°C, the result was a solid "bloom," a spongy mixture of iron and slag. To make wrought iron, the smith heated and hammered this lump over and over, in order to fuse the bits of metallic iron together while forcing out the slag. The smith welded the iron into useful objects by heating the metal until it glowed red-hot and then pounding it into shape (18).

Bloom and wrought iron are distinguished in the Homeric poems. During the funeral games for Patroclus, Achilles produces a "lump of pig iron" (Il. 23:827) for the warriors to throw (19). The Greek word used thrice in this scene is *solos*, which likely refers to the bloom, or unwrought iron, for it bears the adjective *autochoônos*, or rudely fashioned. Elsewhere in the passage the lump is the more common *sidêros*, but the massive size and formlessness of *solos* seems to refer to either a deliberately smelted bloom of iron or perhaps an iron-rich "bear," the aggregate of waste left over from the smelting of copper or lead. Achilles challenges his men to compete for this heavy prize:

> An ingot big enough to keep the winner in iron for five wheeling years. Though his rich estates lie far away in the country, it won't be want of iron that brings his shepherd or ploughman into town— he'll be well-stocked at home. (Il. 23:834)

The bloom is clearly meant to be hauled home by the winner and wrought there into ploughshares that will be superior to the plow of wood traditionally used to turn the fields (20). This highlights the localized nature of the manufacture of uncarburized iron implements: smithing of wrought iron was not a very specialized business, and every estate probably had a worker who could do the job.

In contrast to the *solos autochoônos*, mentioned only in this scene in *Iliad* 23, wrought iron appears throughout both poems. In the *Odyssey*, treasure is depicted by the formula, "bronze and gold and plenty of hard wrought iron" (*chalkos te chrusos te polukmêtos te sidêros*) (14:322 and 21:9) (21). The same formula appears again in the *Iliad* when warriors attempt to purchase their lives (6:47, 10:378, 11:132). This phrase emphasizes the toil expended upon the wrought iron, turning it into such a useful metal that its value stands alongside bronze and gold. Iron is no longer the rustic

raw material for a plowman or shepherd, but a nobleman's ransom—well wrought arms and armor.

Wrought iron can be identified in the texts by its color. Axe heads used in archery contests are described as *ioeis sidêros*—dark violet iron (Il. 23:850) or the more common *polios sidêros*—grizzled or gray iron (Od. 21:9 and 24:164). Although bloom iron is also grayish, in this context the color gray likely indicates that the axe heads are well tended and polished after use with animal fat to keep away the red tinge of rust. Indeed, *polios sidêros* is part of Achilles' war booty, along with "gold, ruddy bronze,/ [and] women, sashed and lovely" (Il. 9:365), that he has won at Troy.

Steel

These iron treasures are so valuable that it is possible they depict not wrought iron, but carburized iron. In the case of the grizzled, gray objects, it seems unlikely, for another type of iron appears in the Homeric texts: *aithôn sidêros*—the gleaming or shining iron more resembling flashing steel. Athena adopts the guise of a sailor trading copper for "gleaming iron" (Od. 1:182). In the *Iliad*, Telemonian Ajax cuts down Simoisius with shining iron (4:485). "Gleaming iron" is brought to a feast, along with bronze, cattle, and slaves (7:472). Finally, Hector vows to fight Achilles, even if Achilles' rage be "burnished iron" (20:371). *Aithôn sidêros* has the appearance of steel and could be what is referred to by the formula "*polukmêtos te sidêros*" (hard wrought iron), since steel, while toilsome to produce, makes a far superior weapon than simple wrought iron.

Archaeological evidence indicates that the advent of consistent, deliberate steeling of iron occurred by 1000 B.C.E., and that production of carburized iron objects increased rapidly after 900 B.C.E. (22). Thus it is likely that audiences hearing the Homeric poems at any time after the 9th C B.C.E. would be able to distinguish the three principal types of iron as well as, or better than, modern readers (23).

Steel, an alloy of carbon and iron, and harder than bronze, is made in three stages: carburization, quenching, and tempering. To make carburized iron, the smith places wrought iron in an oxygen-poor, white-hot fire (above 800° C). The higher the temperature and the longer the iron sits in the fire, the more carbon diffuses into the iron. While cooling in air, the steel adopts a pearlite microstructure, referring to the tiny, alternating layers of ferrite (pure iron) and iron carbide. The smith

then cold-hammers this steel in order to harden it: hammered steel with 1.2% carbon is about twice as strong as bronze (14).

Steel is made even harder by quenching, i.e. plunging the white-hot iron into water. Iron carbide cannot form when iron is cooled so quickly; rather, the carbon is simply frozen in solution in the ferrite, producing the needle-like microstructure called martensite. Martensite is the hardest but most brittle steel (24). Brittleness is not a problem for small objects like arrowheads, which do not need to withstand much force. Nor is brittleness a problem for thick objects like axe heads, for though the exterior turns to martensite—brittle but strong—the interior cools more slowly, producing a pearlite microstructure that reduces the tendency for the thick object to fracture.

The problem of brittleness is the most acute for the sword, a long and thin weapon. The brittleness of a sword is reduced by tempering, or reheating the iron at a relatively low temperature (under 725° C) after quenching. This causes some carbon to fall out of solution as diffuse iron carbide, a modified pearlite. The higher concentration of pearlite reduces both brittleness and hardness at the same time. Tempering is an inexact technology, since the temperatures required for tempering are lower than red or white heat. Without a visible color change of the metal, the ancient smith would have gauged the temperature of the forge and the optimal tempering time by trial and error, and such understanding would then be passed down from master to apprentice in the family trade.

Woodcut, Hans Burgkmaier, Illustrated Bartsch, Vol 11, courtesy Abaris Books, Norwalk, CT.

The process of producing steel objects must have seemed miraculous to the ancients. Not only did the results vary according to apparent chance (the time and temperature of carburization being difficult to quantify), but also the process relied on the elements fire and water. The element fire was difficult to understand in the ancient world, since it works in so many different ways: it reduces or oxidizes ores, depending upon conditions; it fuses glass and clay but breaks down gypsum and limestone. As Pliny wrote in the first century C.E.: "Fire is a vast unruly element, and one which causes us to doubt whether it is more a destructive or creative force" (11, 25).

We find no images of tempering in the Homeric poems, and so cannot infer anything about how fire's action upon iron is understood. We can, however, approach the element water, since the *Odyssey* employs a famous simile of a smith quenching iron. In this simile, iron is compared to the hot, charred spike of olivewood Odysseus and his men ram into Cyclops' one eye:

> as when a man who works as a blacksmith plunges a screaming great ax blade or plane into cold water, treating it for temper, since this is the way steel is made strong, even so Cyclops' eye sizzled about the beam of the olive. (9:393) (26)

Stanford notes that in the Greek of line 393—*pharmassôn: to gar aute sidêrou ge kratos estin*—there is a tension between water's act of hardening iron compared with its more familiar solvent action. *Pharmassôn* "possibly. . .implies an almost magical result of the treatment, a trace of the many early superstitions about iron" (27). Elsewhere in the *Odyssey*, the noun *pharmaka* appears in a medical context, modified by both positive and negative adjectives (4:230), so that it seems not such a great leap to infer that the verb *pharmassô* connotes a "doctoring" of the metal. If so, then the use of *pharmassôn* in Book 9 indicates that water is at least as puzzling an element as fire. Sometimes water softens and dissolves, as in the cooking of food or the washing of dirt from fabric; and sometimes water hardens, as in the miraculous toughening of iron. Although the journeyman smith may not have thought much about water's mystical action upon iron, the puzzlement preserved in the quenching metaphor may have influenced Plato's theory that metals are "fusible kinds of water" (28).

The mysterious powers attributed to fire and water by ancient authors may be less a true reflection of first millennium B.C.E. technological theory than a poetic preservation of the mythology of earlier generations (29).

Archaeological sites in the Mediterranean show evidence of centuries of experimentation with iron during the era of merging of the Homeric texts, resulting eventually in a "broadly based iron economy" (30) with highly skilled artisans. The high regard given to such artisans is implied in two Homeric scenes in which royal or divine metal workers bring the tools of ironworking to fashion precious metals (7). In *Odyssey* 3:432-435, Nestor's goldsmith assembles hammer, anvil, and tongs to gild the horns of a sacrificial ox, when simply wrapping the horns with gold leaf would do. In *Iliad* 18:468-477, Hephaestus fashions Achilles' arms and armor out of gold, bronze, and tin, using impressive but superfluous ironworking tools. If the association of ironworking with royal sacrifice and divine artistry is intentional, the honor given to ironworking in these passages is due to recognition of the exceedingly useful nature of steel, the wondrous technology of its production, or both. Certainly, the association of ironworking with religious ritual is not confined to the Homeric poems. The location of 10th C B.C.E. iron artifacts from Taanach, in Palestine, suggests that smithing or repair of iron objects had a sacred dimension (12), resulting perhaps from some mystical understanding of the metal or from the simple desire of those in power to control a lucrative product.

The Heart of Well-wrought Iron

Why should we care about the complexities of iron in the Homeric epics, other than to satisfy historical curiosity? Reading the *Iliad* and the *Odyssey* with a nuanced awareness of iron enables us to recognize iron's metaphoric richness. Iron is a metal that transforms, shedding some attributes and gaining others under the alchemical influence of fire and water. Iron, like the human heart, can change under the influence of outside forces.

In most instances, "iron-heartedness" calls upon the qualities of hard-wrought iron: strong, impervious to blows. In the *Odyssey*, Telemachus, Calypso, and Odysseus all invoke the iron heart to describe endurance (4:292) or lack of compassion (5:190 and 23:172). Such iron hearts recall the *polukmêtos sidêros*, in that hardness or immovability can be, in many situations, exceedingly valuable. In *Odyssey* 23, for example, Penelope's iron resolve not to yield until she tests Odysseus is as heroic as Odysseus' ability to keep his temper and his beggarly disguise.

The wrought-iron heart is applied to Priam twice in *Iliad* 24. As Priam announces his plan to ransom the body of Hector from Achilles, Hecuba vehemently objects:

> How can you think of going down to the ships, alone,
> and face the glance of the man who killed your sons,
> so many fine brave boys? You have a heart of iron!
> (24:205)

Priam's heart shows the quality of unchangeable resolve, but also a shadow of thoughtlessness; Hecuba implies that wisdom requires a certain pliability of heart, the ability to contemplate a situation from several sides in order to make a prudent choice. In Achilles' camp, Priam's audacious supplication wins Achilles' pity (31). Achilles marvels:

> Poor man, how much you've borne—pain to break
> the spirit! What daring brought you down to the ship,
> all alone, to face the glance of the man who killed
> your sons, so many fine brave boys? You have a heart
> of iron. (24:521)

Priam meets the terrible warrior Achilles without bursting into vengeful anger or shrinking from the risk of violent death. Priam's heart has been wrought like iron: the heat of war and the battering losses of his sons have given him heroic endurance.

Achilles' Heart of Steel

We see Achilles' iron heart transformed during the course of the *Iliad*. Before he dies, Hector begs Achilles to yield his corpse to Troy. Achilles refuses:

> Would to god my rage, my fury would drive me now
> to hack your flesh away and eat you raw— such ago-
> nies you have caused me!

Hector laments Achilles' iron, ruthless heart (22:357). Yet there is a subtle difference between Achilles' heart and the other enduring hearts, which are fixed, immalleable and cool, as if all the iron working is done and we see the finished, hard wrought heart. Achilles' heart is ravenous, as if we catch it being steeled—devouring carbon from the white-hot coal that is the life of his enemy.

Looking back through the epic, we see that the heart of Achilles who sulks by the ships is bloom iron, not well wrought at all, good only for resisting his comrades' entreaties. This heart endures, but its purpose is without benefit to Achilles or his fellow Achaeans. With the death of Patroclus, the heart is hammered and the dross pounded out—it rages in red-hot, bloodthirsty grief, and even the battle with the waters of the Xanthus cannot cool it. This Achilles is wrought iron.

Achilles' heart then lives through the process of steeling. It is carburized and quenched in the blood of Hector, leaving such hardness and brittleness in Achilles' breast that he drags Hector's corpse around Patroclus' tomb day after day. Priam's supplication finally tempers the steeled heart, which gains the suppleness required for yielding Hector's body to Troy with honors. Tempering also imparts wisdom, for only a thoughtful heart recognizes the fragility of the rapprochement: Achilles warns Priam not to make him angry and likewise takes pains not to anger Priam. In other words, Achilles finally becomes aware of the larger environment of his actions, not only of the suffering his rage has inflicted on others, but of the "intertwining and colliding of fates" that unite Priam and Achilles (32).

This evocative image of a steeled heart is important, not only because it helps us deepen our interpretation of two canonical epic texts, but because it tells us something about the history of an important chemical technology. If "iron" in the Homeric epics refers not just to a single static metal, but rather refers to several different forms of iron, then it means that audiences during the so-called Dark Ages knew iron working well. During this period, before writing was invented, the epic stories were fluid, composed during oral performances by the bards, who showed their prowess by spinning skillful similes and metaphors, like the quenching simile in the *Odyssey* and the iron heart metaphors of *Iliad* 24. Oral composers invented these allusions because iron working was familiar enough to function in comparison with other actions or things, and novel enough that the comparison was vivid and lively. Later, with the spread of literacy during the Archaic Period, the role of the bard changed from composition to recitation, essentially freezing the epics—and the most recent similes and metaphors—in several forms that were later standardized. In other words, the metaphors and similes containing references to three types of iron date from the pre-literate, oral composition period, and are not insertions made during a later period. This model accords well with the generally accepted timeline of ancient Greek history: the production of steel is widespread by 900 B.C.E., and the Homeric epics are written in some form by 800 B.C.E. Sharpening our understanding of iron's chemical transformation enables us both to recognize the complexity and variety of references to multiple types of iron in two early literary masterpieces, and to fix the invention of these allusions to an era just prior to the writing of the epics in the ninth century B.C.E.

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19. "Pig iron" is a misnomer in Fagels' translation, since the term refers to ingots of cast iron from a blast furnace. The technology of intentionally melting and then

casting iron did not arise until the 4th C B.C.E. in China and the 14th C C.E. in Europe (J. Needham, "Iron and Steel Technology in East and Southeast Asia," in T. Wertime and J. Muhly, Ed., *The Coming of the Age of Iron*, Yale University Press, New Haven, CT, 1980, 539).

20. H. Hodges, *Technology in the Ancient World,* Alfred A. Knopf, New York, 1970, 155.

21. In the oral phase of epic composition, singers would perform some sections of the well-known stories by heart, relying on epithets, or formulaic descriptions, for familiar people and objects. These phrases, sprinkled throughout the surviving text, reflect the common stock of language and folklore that each singer would improvise upon, like a jazz musician who improvises upon standard tunes.

22. Carburization is determined by observing the microstructure of artifacts by optical and scanning electron microscopy. Intentional steeling of iron implements is indicated if an object can be shown to be uniformly carburized on all sides, and if a group of similar objects from a site shows the same patterning (Ref. 12).

23. Moderns may be less likely than the ancients to be able to identify the stuff of daily objects, beyond such generics as "wood," "plastic," or "metal." First, it is just too difficult to keep track of the incredible variety of materials, both natural and synthetic, we use for buildings, furnishings, and tools. Second, manufacturing processes are not done domestically; most of us have never seen a blacksmith's shop or a sawmill firsthand.

24. P. Craddock, *Early Metal Mining and Production,* Smithsonian Institution Press, Washington, DC, 1995, 126.

25. F. Habashi, "Zoroaster and the Theory of Four Elements," *Bull. Hist. Chem.*, **2000**, *25,* 109-115.

26. The translation of this passage is Lattimore's (R. Lattimore [trans.], *The Odyssey*, Harper Colophon, New York, 1975). It is important to emphasize that the process described in the Cyclopeia is *quenching* (rapid cooling) not *tempering* (reheating), "a point that has been hopelessly confused by modern translators" (J. Muhly, "The Bronze Age Setting," in T. Wertime and J. Muhly, Ed., *The Coming of the Age of Iron*, Yale University Press, New Haven, 1980, 67). A quick survey of the bookshelf proves Muhly's point. "Temper" or "tempering" is used in the translations of this passage by Lattimore, Rouse (W. H. D. Rouse [trans.] *The Odyssey*, Mentor Books, New York, 1937), and Fagels (Ref. 9). Fitzgerald avoids this terminological pitfall: "In a smithy/ one sees a white-hot axe head or an adze/plunged and

wrung in a cold tub, screeching steam—/the way they make soft iron hale and hard. . ." (R. Fitzgerald [trans.], *The Odyssey*, Vintage Books, New York, 1990).

27. W. B. Stanford, Ed., *The Odyssey of Homer,* Macmillan, London, 1965, 361.

28. Ref. 2, p 60.

29. For example, the quenching simile in *Odyssey* 9 likely originated from an older version of the Cyclopeia, a folk tale in which iron played an explicit role (D. Page, *The Homeric Odyssey*, Clarendon Press, Oxford, 1955). According to Page, the Polyphemos episode is one of many universal folk tales woven into the *Odyssey*. The story of the man-eating, giant shepherd has been found in at least 125 versions from diverse cultures, and it is unlikely the *Odyssey* could be the source of all of them. Page identifies certain elements of the tale that are true to the basic plot, and certain elements that are unique to the *Odyssey*. In many traditional versions the giant is blinded with a metal roasting spit, most recently used to cook the hero's companions, rather than the stake of olive wood, as in the *Odyssey*. Page hears an echo of the older tale in the description of the stake that "glowed through terribly" (*diephaineto d' ainôs*, Od. 9:379). An iron spit, he argues, could certainly glow red or white-hot, but a green olive trunk could not, no matter how long it was turned in the fire. The metalworking simile may have existed in the earlier folk tale and been retained, or the iron spit of folklore suggested the vivid image of quenching to the singer or poet, even though he changed the iron spit into a green olive trunk.

30. A. Snodgrass, "Iron and Early Metallurgy in the Mediterranean," in T. Wertime and J. Muhly, Ed., *The Coming of the Age of Iron*, Yale University Press, New Haven, CT, 1980, 335.

31. See J. Kim, *The Pity of Achilles: Oral Style and the Unity of the Iliad,* Rowman & Littlefield, Lanham, MD, 2000.

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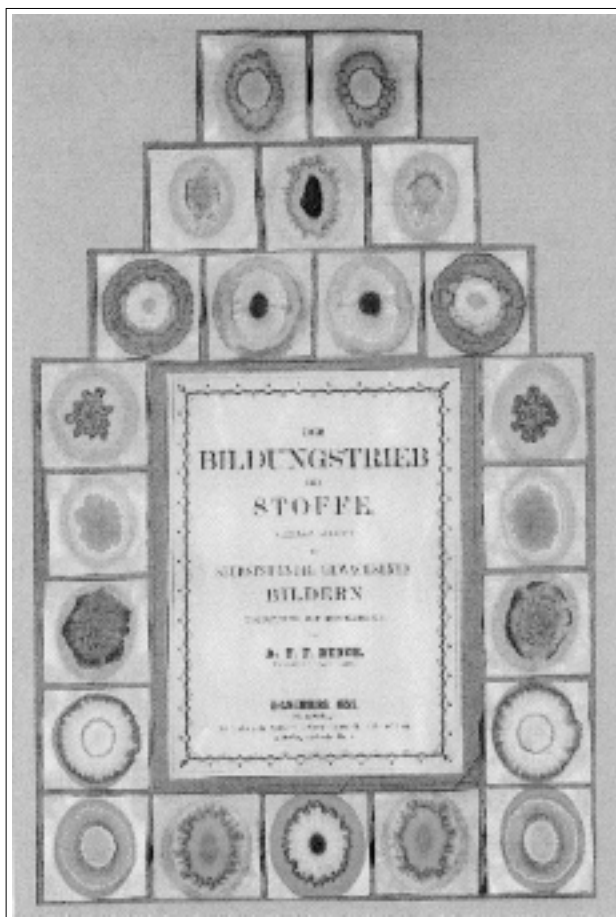
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FRIEDLIEB RUNGE AND HIS CAPILLARY DESIGNS

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The chemical sciences in modern times owe no small debt to the development of improvements in analytical techniques. Chromatographic methods, in particular, have served as successful, systematic separations in chemistry, biology, and biochemistry. The founder of chromatography is recognized as the Russian botanist M. S. Tswett (1), who in 1906 applied the concept of "chromatography" for the first time. In 1941 the work of British chemists A. J. P. Martin and R. L. M. Synge (2) became world renowned; they were awarded the Noble Prize in 1952 for the development of partition chromatography.

By contrast the work of the German chemist F. F. Runge (1794-1867) has remained virtually unknown. About 100 years before Martin and Synge, he took advantage of the capillary action of blotting paper as a means of visualizing chemical changes. In his 1855 book, *Bildungstrieb der Stoffe*, Runge described techniques that are the forerunners of modern paper chromatography.

Title page, Der Bildungstrieb der Stoffe*, Oranienburg, 1855.*

Who was Friedlieb Ferdinand Runge?

The academic and industrial chemist F. F. Runge was born on February 8, 1794 in Billwerder near Hamburg. After completing an apprenticeship in pharmacy in Lübeck, he first studied medicine in Berlin and then moved to the university in Jena, where he concentrated on plant chemistry. In 1822 he completed his doctoral studies on toxic plant extracts, under the direction of W. Döbereiner (3). He became Professor of Technical Chemistry at the University of Breslau (currently

Wrozlaw, Poland) (4) in 1828.

Because he found the meager salary of a professor disappointing, Runge took a position in 1833 at the *Chemische Produktenfabrik* in Oranienburg (5), where he sought the opportunity to bring his creativity and inventiveness to fruition. As technical director, Runge had as one of his assignments finding uses for coal tar oil, a byproduct in the manufacture of illuminating gas (6). In the process he discovered and identified phenol and aniline (7). Much to his surprise, he was able to isolate deep-red crystals from the distillation residue. This *Rosolsäure* yielded a brilliant red dyestuff, the first synthetic textile colorant,

Title page, Musterbilder für *Freunde des* Sch*önen*, *Berlin, 1850.*

Runge informed his supervisors of his discoveries and proposed building a factory in Oranienburg for the manufacture of synthetic dyes and other coal tar products. This took place in 1836, indeed 20 years before the discovery of mauve (8) by W. Perkin (1856). His plan fell on deaf ears at general management in Berlin. He turned to experimenting with stearin and paraffin (9) for the manufacture of candles for domestic illumination, but his proposal to build a candle factory was also denied. Finally, Runge made the suggestion to manufacture "synthetic guano" from bones and other slaughter house wastes for use in agriculture (10). His thought was that the deteriorating fertility of farmland would afford an opportunity for a thriving enterprise and high profits. Once again, however, his message went nowhere.

suitable for dyeing calico and silk fabrics. Further investigations led Runge to the preparation of violet and bluedyestuffs. When cotton fibers were impregnated with aniline and then treated with copper salts and potassium chromate, there appeared a light-fast black, which could be reduced with sulfurous acid to an emerald green.

Runge was bitterly disappointed over the denial of his proposals and the continual disagreements with higher authorities. He accused the ministerial offices of scientific ignorance. In response the executive officers faulted Runge for spending too little time in the factory. In fact, Runge wrote no fewer than seven textbooks (11) during his employment, between 1834 and

Table. Examples of "Runge Designs"

Solution A	"Instrusion Agent"	Solution B	Result
Pb(III) sulfate	—	K ferrocyanide	deep-blue ring with brown border
Mn sulfate	ammonia	K chromate	dark brown ring with light brown border
Cu sulfate	$(NH_4)H_2PO_4$	K ferrocyanide	red core with green border

1850.   The conflict ended in 1851 with his dismissal. As a pension Runge received 400 Taler (12) annually and wood to heat his living quarters. In return, he was required to reside in Oranienburg, "so that one could seek his professional advice at any time."

Capillary Designs "for Friends of Beauty"

At the age of 56 Runge could now turn his attention to a hobby that had long fascinated him: color reactions for identifying single components in mixtures. The kitchen of his bachelors' quarters was converted into a make-shift laboratory, with cups and plates serving as substitutes for glass apparatus. He was able to carry out distillations and concentrations with his coal stove. Having been barred from his former work place, he found it necessary to be very sparing in use of chemicals. In this way he became adept at working with very small quantities of material: this was analysis on a microscale. Not wanting to spend his time cleaning test tubes, Runge came upon the idea of carrying out chemical reactions on the surface of blotting paper. Thus he developed a new field of practical chemistry: capillary analysis.

Runge's technique was conceptually simple: a wooden frame (roughly 12 x 12 cm.) was wrapped with cord on which was placed a piece of unsized, adsorbent paper (*Löschpapier*) (13). He introduced a solution of A dropwise by means of a pipet in the center of the paper, being certain that each drop was taken up individually by the paper. After the paper had been allowed to dry, he introduced a solution of B on the exact same spot. The result was the formation on the paper of deposits in the form of characteristic rings, bands, or irregular shapes. The final appearance could be varied at will by the use of "intrusion agents" ["Störsubstanzen"], such as ammonia, hydrochloric acid, oxalic acid, or a small amount of sugar, egg white, or gum arabic. The resulting "Runge designs" resembled in shape the ameba, jellyfish, or a wreath.

Runge concluded that the circular images arose:

> ..durch eine neue, bisher unbekannte Kraft, die mit Magnetismus, Elektrizität und Galvanismus nichts gemein habe ("from a new, as yet unrecognized force but different from magnetism, electricity, or galvinism.")

He called this force the "creative drive" (*Bildungstrieb*) of matter. Today we recognize Runge as the first to identify the principle of chromatography, a method for separation and identification of chemical substances in a complex mixture.   He did not extend this basic principle to the next logical step-practical analytical applications. After all, in retirement Runge was assigned no scientific projects (14).

Runge's "Picture Patterns" - Rare Curiosities

Runge's enthusiasm for the beautiful "color spots" prompted him to introduce the "spontaneously formed images" to the public. He encouraged Oranienburg school children to assist in preparing the images, and they in turn were thrilled to collaborate with the prominent scholar. Under Runge's guidance, thousands of chromatograms were produced and, together with scientific explanations, used to embellish books, which were printed privately in limited editions between 1850 and 1855 (15). What has become of these books? About 20 of these rarities can be found presently in various libraries, among them:

> Philadelphia (Chemist's Club Library, Chemical Heritage Foundation)
> Philadelphia (Library of the Philosophical Society)
> Oberlin, OH (Library of Oberlin College)
> New Haven, CT (Yale University Library of Rare Books)

In his last years Runge turned his attention to everyday chemistry. He wrote articles of advice on popular and practical science and its basis in daily work. Tradesmen, for example, learned that lumber could be protected effectively against decay by treatment with coal tar oil. Farmers received advice on the disinfection of cow stalls with bleaching powder (chloride of lime), and pharmacists were instructed on the detection of sugar in urine. Most of the articles were addressed to housewives. They learned why wool stockings should not be laundered in hot water and how rust spots could be removed from white fabrics, namely with oxalic acid. In clear but detailed form, he offered recipes for rapid marinating of meat and preparation of an easily digestible cucumber salad. Runge's articles were later published in book form (16), and he was recognized as the "pioneer of popular chemical formulations."

In Oranienburg Runge was considered an eccentric, cranky independent scholar. In 1862, 28 years after his discovery of coal tar dyes, he was honored with a high tribute at the Industrial Congress in London, and he was finally honored in the Prussian capital of Berlin. He was given honorary membership in chemical societies and received several honorary degrees and awards.

After a short illness, Runge died in his residence in Oranienburg on March 25, 1867, where he was buried in the municipal cemetery.

Conclusion

F. F. Runge, one of the first industrial chemists, discovered and isolated the plant alkaloids quinine, atropine, catechol, and caffeine. From coal tar oil he was able to isolate phenol, aniline, quinoline, and thymol. He was far ahead of his time, having proposed large-scale pro-

Runge's residence and place of death, Oranienburg

duction of coal tar dyes, wax candles, and synthetic fertilizer. Had he not been impeded but rather encouraged by the Prussian bureaucracy, he might today be considered the founder of pharmaceutical chemistry and coal tar dyes and fertilizer industries. From his publications, Runge can be considered the discoverer of capillary analysis, developed as an analytical tool 100 years later in the form of paper chromatography.

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3. Johann Wolfgang Döbereiner (1780-1849), known among other things for his lamp and for chemical catalysis.
4. In the cholera epidemic in Breslau in 1831 Runge used bleaching powder for the first time as a disinfectant with great success, thereby earning high respect from the population.
5. The "Chemisches Produktenfabrik" in Oranienburg, north of Berlin, founded in 1802 by the pharmacist G. Hempel, was the most modern chemical factory in Europe at that time. It produced sulfuric acid, hydrochloric acid, soda and in organic pigments. Later a soap factory ("Oranienburger Soda-Seife" was added.
6. The Oranienburg factory used coal gas from coke for thee synthesis of ammonia. This coal gas, supplied by Berliner Gasanstalten, contained residues of coal tar oil, which at the time was of no value.
7. The concept of phenol or aniline was unknown at the time; Runge the substances he discovered as "Carbolsäure (carbo = carbon) and Kyanol (Gr., kyanos = blue).
8. William Perkin (1838-1907) discovered the first coaltar dye mauve in 1856 and began commercial production in 1857, which ushered in the era of synthetic dyes.
9. Runge obtained stearin from imported palm oil and paraffin from domestic peat. Both raw materials were cheaper than beeswax then being used for candle manufacture.
10. The idea to make "synthetic guano" from slaughter wastes originated with J. von Liebig (1803-1873). The first production of synthetic fertilizer was achieved in Heufeld, Bavaria and Wiesbaden, Hessen in 1857. Runge might have begun manufacture and sale of "synthetic guano" seven years earlier.
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12. The Prussian king later granted him an additional 350 Taler annually, in recognition of his contributions to science.
13. The nature of the paper is crucial for the success of the chromatogram. Thin, unsized, highly absorbent cotton or linen paper is recommended. It must be homogeneous and as flat as possible, such that the capillary designs may freely develop.
14. The "Tüpfelmethode"—spot test—developed by the Austrian chemist Fritz Feigl (1891-1971) was but a short step further. Another Austrian chemist, Fritz Pregl (1869-1930), was awarded the Nobel Prize in Chemistry in 1923 for his development of qualitative and quantitative microanalysis.
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Runge with his home made gooseberry wine (Photograph ca 1860, the only one known to exist.)

JOHN HUGHES DAVIES. THE EFFECT OF THE SILENT ELECTRICAL DISCHARGE ON THE AMMONIA SYSTEM*

John T. Stock, University of Connecticut [†]

The Reversibility of the Hydrogen-Nitrogen-Ammonia System

The Haber-Bosch process for the manufacture of ammonia from its elements was a triumph of German science and technology. The commercial production of ammonia by this process began in 1913 (1). Because of its industrial and economic importance, this introduction has tended to overshadow the numerous studies on the basic reaction:

$$N_2 + 3H_2 \rightleftharpoons 2NH_3 \qquad (1)$$

As early as 1785 Claude Louis Berthollet (1748-1822) studied the decomposition of ammonia by electric sparking. He found that 0.725 by volume of hydrogen and 0.275 by volume of nitrogen were produced. Several other workers confirmed this effect of sparking but noted that some NH_3 always remains. The partial formation of NH_3 when mixtures of H_2 and N_2 were subjected to various forms of electrical discharge was also observed. In other words, the system is reversible (2).

The Silent Electrical Discharge

As is obvious from the widespread use of power lines, air—a typical gas—acts electrically as an insulator. If an electromotive force (emf) is applied to a pair of metallic conductors that are separated by a small gap, the flow of current is essentially zero. However, if the emf is progressively increased to very high levels (thousands of volts) and the gap is viewed in the dark, a faint glow, associated with a tiny current flow, becomes visible. This is the region of the *silent electrical discharge*. The glow becomes much stronger and brushlike when the emf is further increased. Eventually, at some critical higher emf, the system enters the highly visible arc or spark region, where the current becomes much larger. This region is easily attained by the use of an induction coil or static electricity generator, but it is difficult to employ quantitatively. The more controllable silent discharge region is preferable for investigative purposes. The discharge is most conveniently produced from an alternating current source, the voltage of which can be readily stepped up as high as desired by use of a suitable transformer.

Effect of the Silent Discharge on the Formation and Decomposition of Ammonia

Several mid-19th century workers investigated the formation and decomposition of ammonia, brought about by the silent electrical discharge. The investigations continued after the turn of the century (3). Despite the several decades of study, it appears that the validity of the law of mass action under such discharge was still an open question. John Hughes Davies, born in Merthyr Tydfil, Wales, carried out experiments aimed at settling the question while at the University of Leipzig.

Davies began his studies on the ammonia system at University College, Cardiff (now Cardiff University). His research director was Edgar Philip Perman (1866-), who had joined the faculty in 1892. Perman was strongly interested in the direct synthesis of ammonia (4) and, with Davies, studied some of its physical constants (5). Davies was also the joint author of studies on the determination of molecular weight (6) and of vapor pressure (7). When he arrived in Leipzig, he was therefore a skilled experimenter, had first-hand experience with the ammonia system, and was well acquainted with relevant literature. It is therefore not surprising that he was able to carry out his extensive examination of the effect of the silent discharge on the ammonia system in the short period between Easter, 1907, and Whitsun, 1908 (8).

Figure 1 *Apparatus used by Davies*

Davies arrived in Leipzig at a time of significant change. Wilhelm Ostwald (1853-1932) had retired from the University in 1906. His successor as professor of physical chemistry was Max Le Blanc (1865-1943), who had been one of Ostwald's assistants from 1890 to 1896. Le Blanc then became director of electrochemistry at the firm of Farbenwerken Hoechst until 1901, when he joined the faculty of the Technische Hochschule in Karlsruhe (9). He returned to Leipzig in 1906, this time as successor to Ostwald, and remained there until his retirement in 1933. Le Blanc directed the work carried out by Davies (8, 10). Davies was fully aware of a recent study that covered, at least from the experimental point of view, much of the area that he proposed to attack. This study was by Robert Pohl (1884-) at the University of Berlin (11). Davies pointed out that, although Pohl recognized the dependence of the decomposition of ammonia on various physical factors, the study was to see whether Faraday's law applied in the silent discharge reaction. Pohl's experiments showed that, under

these conditions, this law was invalid. The principal concern of Davies was the validity, or otherwise, of the law of mass action under similar conditions.

The experimental arrangement used by Davies, shown in Fig. 1, is similar to that used by Pohl. Davies stated that the reaction vessel was a Siemens ozonizer tube. However, it seems obvious from Fig.1 that the tube was of the so-called Brodie form, shown schematically in Fig. 2. The shading indicates mercury and dilute H_2SO_4, which act as the actual electrodes for the electrical discharge. Several tubes were used, so that, in the narrow annular space, the volume of gas varied between 20 to 30 ml and the path length through the gas between approximately 1 and 2 mm. This narrow space can be evacuated to permit the introduction of the gas, and suitable stopcocks control the various functions. The three-way stopcock D permits the isolation of the major portion of the system, evacuation, or release of the vacuum by entry at N of air, dried by the system N, Z. Bulb Q contains either nitrogen or hydrogen, which passes through drying system P, O before use. The gentle heating (even by hand!) of normally refrigerated solid AgCl (2NH$_3$), contained in vessel G, generates ammonia. This is dried by passage through the system Y, X, which is cooled by an ice-salt mixture. In
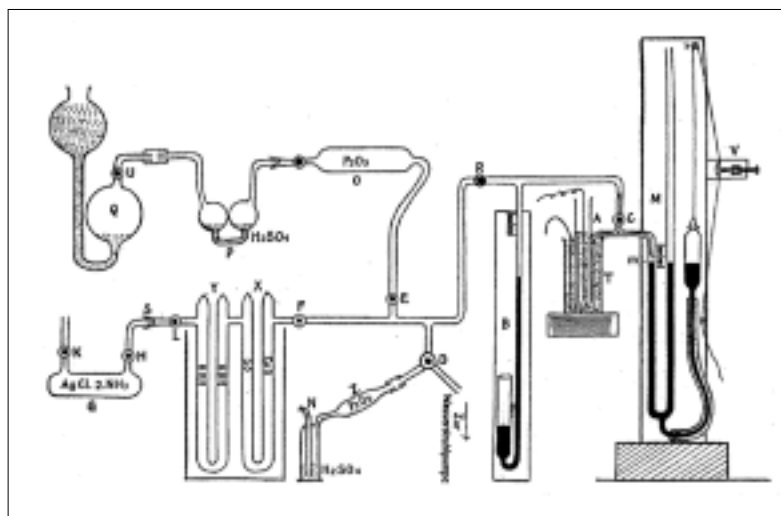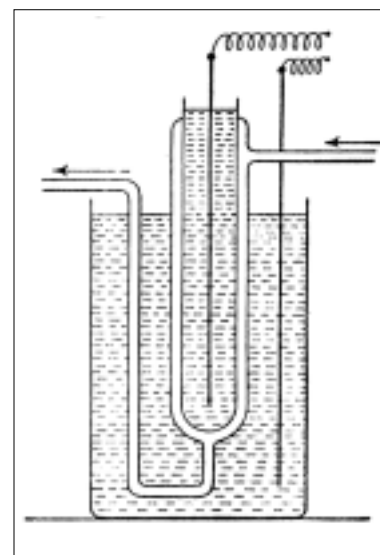

Figure 2 *Ozonizer tube*

experiments where the gas pressure is kept constant, the mercury level in the left-hand limb of Manometer M is maintained at mark *m*. The capillary connection between A and M keeps the dead space small. Manometer B is used to control the filling of the ozonizer tube with the desired gas.

High-voltage alternating current is applied to the ionizer tube by wires that dip into the liquids, as indicated. The heights of these liquid electrodes govern the volume of gas subjected to the discharge. The glass surfaces are rendered nonconducting by a coating of shellac. The approximately 140-V output of a rotary dc-to-ac converter could be stepped up to as high as 10,000 V by a transformer. The applied voltage is measured by a precision voltmeter, connected through a mercury switch and a high resistor. The voltage drop across a smaller resistor, placed in the lead to the inner contact, is measured by a quadrant electrometer. This permits the estimation of the current passing through the gas. This current is actually the sum of the current that passes through the gas and the *Aufladungsstrom* (charging current) of the tube. The latter current, determined at several voltages after evacuation of the tube, is deducted from the total current. When the volume of gas is kept constant, any reaction that occurs can be indicated by change in pressure, measured by manometer M.

Figure 3 *Decomposition constants at fixed current levels.*

Pohl had observed and Davies confirmed that the gases must be dry. Ammonia (NH_3), stored as $AgCl(2NH_3)$, is released as required by warming. Nitrogen and hydrogen, stored in glass flasks, are with-

drawn as needed. To prepare a N_2-H_2 mixture in stoichiometric proportions corresponding to NH_3, ammonia was strongly heated over iron or nickel. The residual NH_3 was absorbed by dilute sulfuric acid. Davies justified his working at ambient temperature by showing that the rate of decomposition of ammonia is comparatively insensitive to temperature.

Because the nitrogen-hydrogen-ammonia system is reversible, the decomposition of NH_3 was limited to not more than 10% to minimize the influence of the reverse reaction. The general method was to keep the volume of gas constant and to assess the extent of decomposition from the change in pressure. Before each experiment the reaction tube was thoroughly dried by repeated evacuation and entry of dry air, while being heated to 300° to 400°. After cooling and introduction of ammonia, the mercury level in the left limb of manometer M was brought to mark **m**. Then the level of mercury in the right limb of M (the initial pressure of NH_3, A_0) was noted. Alternating current of known strength was then switched on and the successive timed readings of M (*total* pressures at times *t*, *A*) were taken.

In order to calculate the decomposition constant of the reaction, the pressures A_t of *ammonia* at times *t* are needed. When two molecules of ammonia decompose, they give four molecules of products. Accordingly, At $= 2A_0 - A$ and with this information, the values of K_1 and of K_2, the respective constants for a unimolecular and for a bimolecular reaction, can be calculated. Figure 3 is a table, reproduced from Davies's paper, which gives results for two current strengths. The results show that the constants are highly dependent upon the current strength and that the values of K_2 change considerably with time. On the other hand, the values of K_1 shift
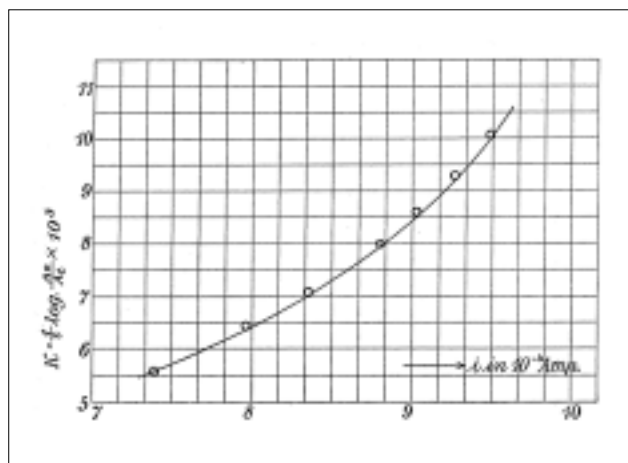

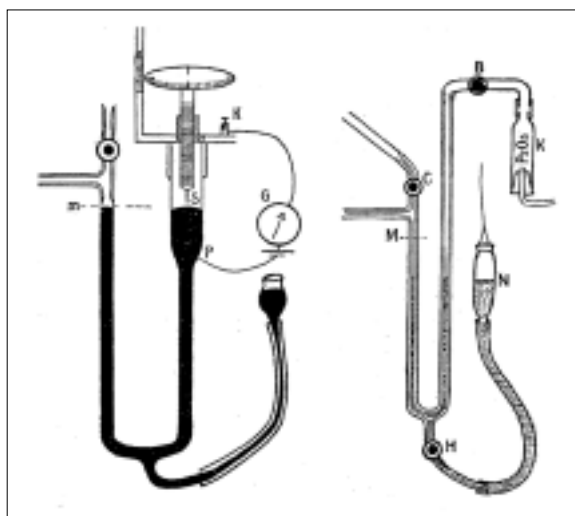**Figure 4** *Relationship between decomposition constant and current strength*

Figure 5 *High-sensitivity manometers*

only slightly. Thus the evaluation of K_I should be a reasonable criterion for comparison in subsequent experiments. The effect of current strength on the value of K_I was investigated more fully, with the results graphed as indicated in Fig. 4. Davies described this curve as being approximately linear, so that K_I can be regarded as being proportional to the current strength.

To examine the effect of pressure of ammonia on the "constant," K_I, two sets of experiments were performed, one at a constant current of 1.3 mA, the other at a constant voltage of 7216. From his findings, Davies concluded that the results of subsequent experiments should be comparable if constant current is used, but not if voltage is the chosen fixed quantity.

Because the ultimate aim of the investigation was to check the validity of the law of mass action, an obvious approach was to study the decomposition of ammonia after mixing it with one of its decomposition products. The system used by Davies allowed such mixtures to be made for subjection to the silent discharge. His results showed that K_I decreases as the $H_2 : NH_3$ ratio is increased. On the other hand, an increase in the $N_2 : NH_3$ ratio brings about an increase in the value of K_I. If the excess of nitrogen is large, the constant can be much larger than for ammonia itself. Davies noted that, with excess hydrogen, the luminescence was yellowish. In the presence of an excess of nitrogen a very strong violet color appeared.

The reversibility of the ammonia system implies that equilibrium could be reached either by the decomposition of ammonia or by its formation from its elements. In his experiments on the formation of ammonia, Davies found that the pressure changes were too

small to be measured by a conventional mercury manometer. For most of these experiments he used the high-sensitivity mercury manometer shown on the left of Fig. 5. With the fine adjustment provided for the height of the leveling bulb of the manometer, pressure changes could then be read to approximately 0.05 mm. The alternative manometer on the right was of conventional form, but filled with an oil of specific gravity 0.895. The lower end of the screw of the micrometer reading device of the manometer carries a platinum spike S. A battery in series with galvanometer G causes the latter to deflect when the tip of the spike just touches the mercury surface.

The experiments were carried out at constant volume, i.e., the level of mercury in the left-hand limb of the manometer was kept at mark **m**. Because pressure changes were small, the equilibration of temperature was particularly important. For the equilibrium study with a stoichiometric mixture of nitrogen and hydrogen, the pressure was read and the constant current was turned on. The process was continued until the pressure showed no further change. Three determinations were made, with initial pressures in the range 757.7 to 764.0 mm Hg. The ammonia so formed ranged from 2.83 to 2.88%. Using the same reaction tube, Davies approached the state of equilibrium by decomposing ammonia. He found 2.87% of ammonia in the final mixture.

The results of similar studies involving a wide range of $N_2 : H_2$ ratios are tabulated in Fig. 6. Clearly, a mixture with the stoichiometric $N_2 : H_2$ ratio of 1:3 gave the highest equilibrium amount of ammonia. Despite the wide range of mixtures, the change in voltage (and hence in energy input, since the current is constant) did not exceed 20%. However, the widely varying values in column 4 show that the law of mass action does *not* hold for the system under silent discharge. Davies commented that very little was known of the process taking place in the tube and, for the present, the matter should be left with the statement of the invalidity of the law of mass action.

Davies examined the rate of formation of ammonia from stoichiometric mixtures. In all cases the initial pressure was 760 mm when timed runs were made at a constant current of three different levels. The results, depicted graphically in Fig. 7, show that ammonia is formed most rapidly in the early stages of the runs. This conclusion was confirmed by a run lasting only one minute, with observations at 5-second intervals.

The final set of experiments involved mixtures in which the $N_2 : H_2$ ratio lay between 1 : 7 and 4 : 1. The

Initial pressure mm Hg	N$_2$: H$_2$ ratio in the mixture	NH$_3$ formed mm Hg	$\dfrac{[N_2][H_2]^3}{[NH_3]^2}$	Potential Volt
740	1 : 20	14.04	457 x 10^4	8528
740	1 : 12	16.05	544	8592
740	1 : 5	19.53	603	8674
760	1 : 3	21.08	636	8774
740	2 : 5	19.50	653	8838
740	2 : 3	16.02	837	8928
740	7 : 6	12.08	892	8976
740	9 : 1	1.48	1085	9184
740	10 : 1	1.26	1180	992

Figure 6 *Equilibrium studies with differing nitrogen:hydrogen ratios.*

constant current runs were terminated at 6 minutes. The rate of formation, [NH$_3$] / time, was 0.88 with a gas ratio of 1 : 7, but fell to 0.45 when the gas ratio was 4 : 1.

Davies concluded that he had shown the decomposition of ammonia by the silent electrical discharge to be essentially a reaction of the first order. The decomposition constant, approximately a linear function of the current strength, has a temperature coefficient much smaller than those of chemical reactions in general. Approximately 3% of ammonia remains when equilibrium is reached. The same percentage is obtained in formation experiments with a stoichiometric mixture of nitrogen and hydrogen. However, the percentage of ammonia formed is smaller in nonstoichiometric mixtures and the results *do* not fit the requirements of the law of mass action.

The decomposition velocity is decreased by an excess of hydrogen and increased by an excess of nitrogen. These effects are reversed in formation experiments. The luminescence associated with the discharge is normally pale but becomes vividly violet when nitrogen is in excess. Davies speculated that this light might be the cause of the accelerating effect of nitrogen on the rate of decomposition of ammonia. The effect of light on various other chemical reactions was well known; and a photochemical reaction often has a small temperature coefficient, like that found in the ammonia experiments.

Davies was granted his Ph.D. in 1908 for these studies, which apparently he did not pursue further. In fact, an author search in the decennial indexes of *Chemical Abstracts* for the period 1907 to 1936 revealed only two

entries for "J. H. Davies." Both concerned methods for welding. In a less extensive survey of *Chemisches Zentralblatt*, no further entry that could be attributed to John Hughes Davies was found. Although he may have continued to undertake research, it appears that he did not publish the results.

Davies returned to the United Kingdom. When he became a member of the Chemical Society in 1910, he stated that he was Vice President of St. Peter's College in Peterborough His name is listed in the Society's Register of 1936 but is absent in the next Register, not pub-
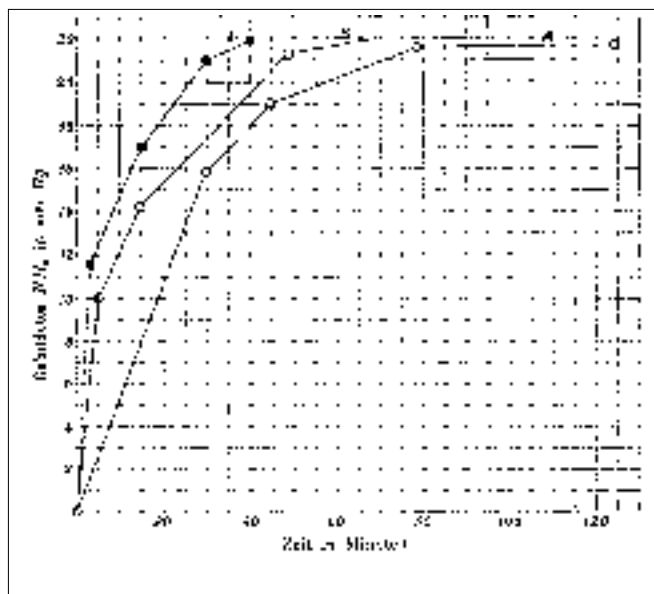

Figure 7 *Rate of formation of ammonia in a stoichiometric mixture. Current, mA:- curve A, 0.84; curve B, 1.54; curve C, 1.80.*

lished until 1948. The University of Cardiff could provide no information concerning Davies.

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THE HISTORY OF CHEMICAL EDUCATION AT LAFAYETTE COLLEGE

Roger A. Egolf, Pennsylvania State University

This paper is an overview of chemical education at Lafayette College in Easton, Pennsylvania from its founding up to the present day, but with emphasis on the curriculum, faculty, and students of the 19th century.

Founding

Lafayette College owes its origin primarily to James Madison Porter, an attorney, judge, and railroad founder who also served as Secretary of War under President John Tyler. Porter was born in 1797, the youngest son of the Revolutionary War General Andrew Porter. His brother David was Governor of Pennsylvania and another brother, George, was the Governor of Michigan. Porter's sister, Eliza Ann, was the mother of Abraham Lincoln's wife, Mary Todd. James Porter persuaded the legislature of Pennsylvania to grant a charter to Lafayette College on March 9, 1826; but it was not until May 9, 1832 that classes were first held. He served as the president of the board of trustees of Lafayette for the first 25 years of its existence (1, 2). The school was not originally church-related, but all the early presidents and board members, and nearly all the early faculty were members of the Presbyterian Church. In 1849 the college formally aligned itself with that denomination, and the charter was modified in 1854 to reflect this affiliation (3).

Until 1865 Lafayette offered only one curriculum, an A.B. degree based mostly on Latin and Greek literature and religion courses. Most of its early graduates became ministers, attorneys, or physicians. Chemistry, included in the curriculum from the founding of the college, consisted of only two terms of study in the junior and senior years until 1853, when it was reduced to one term in the senior year (4).

The first professor to hold the chemistry chair at Lafayette was Samuel David Gross, M.D. Born on his father's farm near Easton on July 8, 1805, he studied medicine at the recently founded Jefferson Medical College in Philadelphia. After graduation in 1828, he practiced medicine in Philadelphia for three years, then returned to Easton where he practiced, studied, and carried out experiments on dogs relating to gunshot wounds of the abdomen. In 1832 he became the first faculty member appointed to the new Lafayette College as Professor of Chemistry, Mineralogy, and Botany; but he never actually taught a chemistry course. He said in his autobiography that he would not have accepted the position if he had actually been required to teach chemistry because he had never made chemistry a "special study." In 1834 Gross resigned his position at Lafayette to become Demonstrator of Anatomy at the Medical College of Ohio and then was appointed Professor of Pathological Anatomy at the Cincinnati Medical College upon its founding in 1835. He subsequently took positions at the University of Louisville in 1840 and fi-

nally at Jefferson Medical College in 1856. Gross, considered to be one of the finest surgeons in the world in his day, was the founder of the Philadelphia Pathological Society, the Philadelphia Academy of Surgery, and the American Surgical Society. Among the many honors he received was the

Traill Green, M.D.

degree of D.C.L. from Oxford University and the L.L.D. from the University of Pennsylvania. Samuel Gross died in Philadelphia on May 6, 1884 (5, 6).
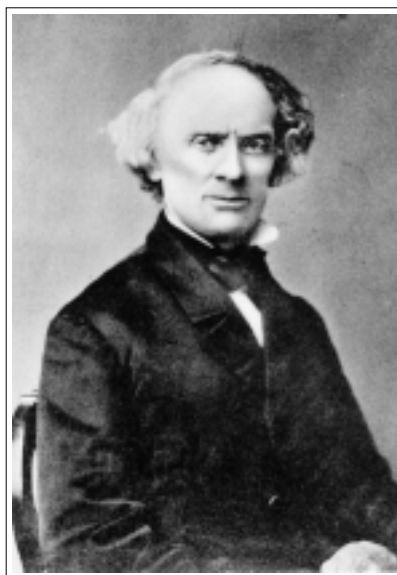
The second faculty member to hold the chair in chemistry was Traill Green, a physician who immediately after graduation with an M.D. from the University of Pennsylvania in 1835 at the age of 22 went into private practice in Easton. In 1837 he joined the faculty of Lafayette, but left in 1841 to take the Chair of Natural Sciences at Marshall College (now Franklin and Marshall College) after a dispute with the Lafayette Board of Trustees over the faculty's authority to discipline students. Green was also a trustee along with serving as a professor, but was strongly on the side of the faculty in this conflict. He taught at Marshall until 1847, at which time he returned to Easton to resume his medical practice (7, 8).

From the date of Traill Green's resignation until he rejoined the Lafayette faculty in 1853, chemistry was taught successively by professors with no formal chemical education. From 1841 until 1845, chemistry was taught by David P. Yeomans, M.D., the brother of the then president of Lafayette, Rev. John W. Yeomans. In the 1845-1846 academic year E. Thompson Baird, an attorney and Presbyterian minister, taught the subject. From 1846 until 1851 the duty of teaching chemistry was carried out by Lafayette's Professor of Mathematics and Natural Philosophy, James H. Coffin. Coffin has also been described as the father of American meteorology (9). In 1851 Coffin became vice-president of

the college, and no chemistry instruction was held for one year (4).

Traill Green rejoined the Lafayette faculty in 1853 and taught chemistry until 1874. From 1865 until 1874 he held the Adamson Chair of General and Applied Chemistry. After 1874 he continued on the faculty but no longer taught courses. He became Dean of the Pardee Scientific Department in 1881, remaining in that position until 1890 when he became acting president of the college. Upon retirement in 1891 he became Emeritus Professor of Chemistry. He also served as a trustee of the college from 1881 until his death in 1897 (4,10).

Scientific and technical education at Lafayette began on a large scale in 1865 with the founding of the Pardee Scientific Department. The driving force behind its founding was Ario Pardee, a self-made millionaire whose principal business was coal mining in Hazelton, Pennsylvania. Pardee saw the need for technically trained employees in the new industries of the late 19th century and initially donated $20,000 to the college and subsequently an additional $100,000 to fund the founding of a scientific school (11). He later underwrote the construction of a large building, Pardee Hall, to house technical education at Lafayette. The new degrees offered within the Pardee Scientific Department were B.S. or B.Ph degrees in general science and chemistry, C.E. (civil engineering), and E.M. (mining engineer) (4,12).

The first building used specifically for chemical education was Jenks Hall, built in 1865 at a cost of $22,000 and named after Barton Jenks, who had donated $10,000 towards its construction (13). Jenks, who lived in Bridestown near Philadelphia, was the son of a former trustee of the college and a manufacturer of machinery for the textile industry. Except for a few years when it was used by biology, it served the Chemistry Department until 1902, when it was renovated for permanent use by the Biology Department. After that department moved into a new building in 1969, it housed the Art and Music Departments. In 1986 it was renovated again and renamed the William E. Simon Center for Economics and Business after the 1952 Lafayette graduate and trustee who financed the renovation and who is best known as a former U.S. Secretary of the Treasury.

Pardee Scientific Department

With the founding of the Pardee Scientific Department and the retirement of Traill Green from teaching, Lafayette needed a new chemistry professor with the

professional reputation to attract science students to the school. That turned out to be Thomas Messinger Drown. He was born in Philadelphia on March 19, 1842, the youngest of three sons of William Appleton Drown, a manufacturer of umbrellas, and Mary Pierce Drown (14). The young Drown

Jenks Hall

woman, Helen Leighton, whom he married in 1869 at her parents' home in Leamington, England. After their honeymoon, Drown returned to America with his wife and accepted the first instructorship in metallurgy at the Lawrence Scientific School of Harvard. He left this position after only one year to work as an analytical and consulting

was an excellent student, eventually graduating in 1859 from Central High School, the first public high school in Philadelphia. Drown's chemistry professor at Central was Martin Hans Boye, the well-known former assistant to Robert Hare and later consulting chemist in partnership with the even better known James Curtis Booth. Booth had preceded Boye as chemistry professor at Central (15).

After graduating from high school in 1859, Drown continued his education as a medical student at the University of Pennsylvania, where he graduated in 1862 with an M.D. after writing a 337-page thesis entitled "An Essay on Urological Chemistry." Upon graduation he took a job as a surgeon on a packet steamer that traveled between Philadelphia and London. He evidently did not enjoy this job because he resigned after only one round-trip voyage and never practiced medicine again. Instead, he decided to return to his favorite subject in both high school and medical school: chemistry (16).

He first went to the Sheffield Scientific School at Yale where he studied with George J. Brush and Samuel Johnson but soon left to study at the Lawrence Scientific School of Harvard, where he spent two years working under the direction of Oliver Wolcott Gibbs on the problem of separation of rare earths. Drown considered Gibbs to be his primary mentor (16, 17).

In 1865 he left Harvard and sailed to Europe where he studied first at the School of Mines at Freiburg with Karl Plattner and later at Heidelberg with Bunsen. He never did receive a degree from either German institution. While he was in Heidelberg, he met an English

chemist with Dr. Frederick Augustus Genth, a Marburg D. Phil., who had worked as Bunsen's assistant from 1845 through 1848 before emigrating from Germany to America. Genth had also served as an assistant to J. W. Gibbs at Yale and was eventually president of the American Chemical Society in 1880. Drown worked in this capacity for four years until accepting the Adamson Professorship in Analytical Chemistry at Lafayette in 1874 (10).

During his years at Lafayette, Drown published extensively on analytical methods for use in the iron and steel industry, with most of his papers appearing in the *Transactions of the American Institute of Mining Engineers*, an organization of which he was a founding member, secretary (1873-1883), and president (1897-1898) (17). Drown alone wrote most of the papers published between 1873 and 1883, but several written after 1879 were co-authored by Porter W. Shimer, a former student who had graduated from Lafayette with an E.M. (mining engineer) degree in 1878.

Besides donating the funds to found the Pardee Scientific Department, Ario Pardee also provided $250,000 for Pardee Hall, a five-story building 256 feet long, which was built between 1871 and 1873 to house the new technical school. The total cost to build and equip the hall was nearly $300,000. Upon completion of this building, chemistry instruction was moved from Jenks Hall into Pardee Hall (18).

On June 4, 1879 disaster struck. Fearing he would be late for chapel, a chemistry student in a laboratory class supervised by Dr. Drown's assistant, Edward Hart,

put a red-hot retort and oily coveralls into his lab drawer at the end of the day. By the time the fire was brought under control, nothing of the magnificent building remained except for an intact foundation, the

Thomas Messinger Drown

radiators, and a pile of stones that could be reused in the rebuilding. Rushing to the building, Dr. Drown managed to save the correspondence of the American Institute of Mining Engineers, along with the only complete copy of the *Transactions* of the society. By the time the AIME's documents were removed, however, there was no time for Drown to save his personal library, worth an estimated $5,000. The membership of the society was so grateful that a committee of its officers, led by coal baron Eckley Coxe and Lafayette professor Rossiter Raymond, raised enough funds for a complete replacement of Drown's books and instruments. Reconstruction of Pardee eventually cost $130,000 (19).

The professors in the Classical Department of the college, already uneasy about the new technical school, immediately blamed technical education in general and Dr. Drown in particular for the fire. Chemistry laboratory instruction and Professor Drown's office were moved into the basement of McKeen Hall, a dormitory that had earlier been called Central House. After Pardee was rebuilt, the administration would not allow chemistry to move back in, so it was forced to remain in McKeen until after Drown resigned in 1881. At this time the technical school was under heavy criticism from the classical professors for being expensive to run and for not attracting enough students. Drown proposed a course in metallurgy, but the trustees never even gave him the courtesy of a reply. The battle came to a climax when Drown resigned at commencement in 1881. He had very strong supporters on the faculty and among the alumni and students. Assembled that same evening in a special meeting, the alumni prepared a petition asking the trust-

ees "to use every legitimate means to retain Dr. Drown" (20).

Drown agreed to withdraw his resignation and accept a year's leave of absence, provided he be able to keep a private laboratory and office in McKeen. The trustees agreed to this but later changed their minds, objecting to odors and increased fire insurance rates. Under these conditions, Drown resigned in the fall of 1881. Simultaneously, three other faculty members resigned in sympathy: Dr. Rossiter Raymond, Professor of Mineralogy and Geology, Dr. Frederick Prime, Professor of Mining and Metallurgy, and Allen Berlin, Adjunct Professor of Mathematics. Berlin later rejoined the faculty. After his resignation, Drown returned to the private practice of chemistry, both in Easton and in Philadelphia. He briefly took over the family umbrella manufacturing business after it had fallen on hard times because of the death of his father and illness of his brother. Drown kept the enterprise afloat long enough to liquidate it and save the firm from bankruptcy (16). Interestingly, even though it was Edward Hart who was actually supervising the laboratory section where the fire originated in Pardee, no one seems to have blamed him, and he was promoted into the Adamson Chair upon Drown's resignation.

In 1883 Lafayette's president of the previous twenty years, Dr. William Cattell, announced his retirement. There was a strong movement by the supporters of Drown to have him chosen the next president of the college; but Cattell, a prominent member of the anti-Drown contingent, and the trustees moved quickly to name James Hall Mason Knox, a Mental and Moral Philosopher to the post. Thus the classicists retained power over the institution (21).

Drown's supporters made one last effort to place him on the board of trustees that year. A petition requesting his appointment was signed by many prominent alumni and every member of the graduating class, but the trustees could not bring themselves to add Drown to their group (22). This decision cost the college the financial support of many wealthy alumni for several years

Pardee Hall burned a second time on December 18, 1897 as a result of arson by George Stephens, a disgruntled former professor of Moral Philosophy and Ethics, who had been fired a year earlier (23). Rebuilt a second time, it is now occupied by humanities departments.

In 1885 Drown moved to Cambridge, Massachusetts to become Professor of Analytical Chemistry at the Massachusetts Institute of Technology. Three years later he became head of the Chemistry Department, and in 1893 he also took charge of the chemical engineering curriculum. Drown was elected president of Lehigh University on April 9, 1895, and remained in that position until his death in 1904 (16, 17).

With the founding of the Pardee Scientific Department in 1865, the college added a B.S. degree, which required no classical language. If a technical student added Latin to his curriculum, the degree awarded was a B.Ph. That year a three-term chemical course was offered as a specialization within the B.S. or B.Ph. In 1868-1869 the chemical course was expanded and given a separate curriculum for the junior and senior years, and by 1876-1877 a full four-year program in chemistry was added. The degree awarded in chemistry was changed to A.C. (analytical chemist) in 1874-1875, but again became a B.S. or B.Ph. in 1879-1880. The B.Ph. was discontinued in 1918, and from then on the only undergraduate degree offered in chemistry was the B.S (4).

The chemistry curriculum was fairly constant during the late 19th century, but did change gradually as the science matured. Reproduced below is the curriculum leading to the A.C. degree that appeared in the Lafayette College Catalogue in the academic year 1876-1877 (24).

Graduate studies were instituted at Lafayette at about the same time as the founding of the Pardee Scientific Department. The Master of Science degree was conferred upon any graduate of the Scientific Department who pursued for two years the post-graduate course of the college in any of the scientific departments, or who had elsewhere for three or more years engaged in scientific pursuits, and during that time sustained a good moral character. Beginning in 1874, a Ph.D. could be conferred by vote of the faculty upon graduates of the college who spent three years in resident post-graduate studies, passed a special examination, and wrote a thesis (25). At some point in the 1880s graduates of other institutions became eligible for admission as graduate students (4).

The first graduate student in chemistry at Lafayette, A. F. Bechdolt, was in residence for the academic year 1867-1868 but did not receive a degree. The first Ph.D. in chemistry was awarded in 1875 to William McMurtrie. McMurtrie, born on March 10, 1851 in Belvidere, New Jersey, was a 1871 Lafayette graduate in mining engineering who spent the 1871-1872 year as a chemistry graduate student. He does not appear to have satisfied the three-year residency requirement, but by 1873 he was the chief chemist of the U.S. Department of Agriculture. He was the 1900 president of the American Chemical Society, a professor of chemistry at the University of Illinois from 1882 until 1888, and also served as a Lafayette College trustee from 1906 until 1912. He died on May 24, 1913 (26).

By 1899, eight individuals had been awarded an in-course Doctor of Philosophy degree in chemistry. Only one of these actually spent three years as a graduate student. The Ph.D. remained on the books until 1918, although no doctorate in chemistry was awarded after 1899 (4, 27, 28, 29).

Faculty

Thomas Drown was succeeded as the head of Lafayette's chemistry department by Edward Hart, who was born in Doylestown, Pennsylvania on November 18, 1854. He had been a special student of chemistry under Professor Drown in his private laboratory in Philadelphia and came to Lafayette in 1874 as Drown's assistant in chemistry. Although he never formally studied chemistry at the undergraduate level, Lafayette awarded him an honorary B.S. degree in 1874. The following year he was appointed Tutor in Chemistry at Lafayette and served in that position until Professor Drown arranged for him to receive a fellowship at the newly organized Johns Hopkins University. From 1876 until 1878 he was a graduate student of Ira Remsen at Johns Hopkins and in 1879 was awarded the first Ph.D. degree in chemistry from that institution. He returned to Lafayette as Adjunct Professor of Chemistry in 1878 and was named Adamson Professor in 1882, a position he held until his retirement in 1916. Hart was a co-founder with J. T. Baker of the Baker and Adamson Chemical company. After the General Chemical Company bought that company in 1913, Hart remained to manage the plant until 1915. Upon his retirement from Lafayette in 1916, he became Vice-President and General Manager of the Clinchfield Products Company at Johnson City, Tennessee. Returning to Easton in 1918, he founded his own company, Hart Laboratories. On the 50th anniversary of his association with Lafayette, the college awarded him an honorary Doctor of Laws degree. Professor Hart won the John Scott Medal of the Franklin Institute for the invention of a wax-lined bottle for the storage of

CHEMISTRY CURRICULUM IN 1876-1877

CHEMICAL COURSE.

FRESHMAN YEAR.

FIRST TERM.

Chemistry, with laboratory Practice.   English. French.
Harmony. Elementary Drawing.   Coleman's Biblical Geography.
Algebra, (completed.)   Old Testament in English.

SECOND TERM.

Chemistry, with Laboratory Practice.   German and French.
Drawing, Plane Problems.   Coleman's Biblical Geography.
Geometry, (completed.)   Old Testament in English.

THIRD TERM.

Analytical Chemistry.   German and French.
Trigonometry and Mensuration.   Coleman's Biblical Geography.
Geometrical Drawing.   New Testament in English.

Throughout the Year—Declamations and Themes.

SOPHOMORE YEAR.

FIRST TERM.

Analytical Chemistry.   German and French.
Geometrical Drawing.   English. French on Words.
Mineralogy.   Acts of the Apostles.

SECOND TERM.

Analytical Chemistry.   German.
Botany and Zoölogy.   French.
Mineralogy.   Acts of the Apostles.

THIRD TERM.

Analytical Chemistry.   Botany.
Determinative Mineralogy.   Zoölogy.
French and German.   Acts of the Apostles.

Throughout the Year—Declamations and Themes.

JUNIOR YEAR.

FIRST TERM.

Analytical Chemistry.   German.
Practice with the Blow Pipe.   French.
Lithology.   New Testament Epistles.

SECOND TERM.

Analytical Chemistry.   Physics.
Practice in Lithology.   Assaying.
Geology.   New Testament Epistles.

THIRD TERM.

Analytical Chemistry.   Physics.
Geology.   New Testament Epistles.

Throughout the Year—Declamations, Themes and written Debates.
Text books in Chemistry in the German language are used during the year.

SENIOR YEAR.

FIRST TERM.

Analytical Chemistry.   Physiological Chemistry.
Chemical Technology.   Toxicology.
Metallurgy.   Rule of Faith.

SECOND TERM.

Analytical Chemistry.   Political Economy.
Chemical Technology.   Agricultural Chemistry.
Metallurgy.   Evidences of Christianity.

THIRD TERM.

Analytical Chemistry.   History.
Chemical Technology.   Graduation Thesis.
Metallurgy.   Butler's Analogy.
Gas Analysis.

Throughout the Year.—Themes and Speaking.
Text books in Chemistry in the German language are used.

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hydrofluoric acid. He also invented the Hart condenser, used in both the United States and England during World War I for condensing the large amounts of nitric acid necessary in making nitroglycerin and gun cotton. Founder of the *Journal of Analytical and Applied Chemistry* in 1882, he is also well known as the second editor of the *Journal of the American Chemical Society* from 1892 until 1901. Professor Hart died in his home on the Lafayette campus on June 6, 1931 (30, 31, 32).

Hart's best known student was probably John Townsend Baker. Baker, born in Orange, New Jersey on June 30, 1860, received a B.S. degree in chemistry from Lafayette in 1882 and an M.S. in 1884 (31). During his senior year he went into partnership with Hart in the manufacture of pure chemicals. In 1884 another of Hart's students, George P. Adamson, joined them and they began to use the company name Baker and Adamson (32, 33). Adamson's uncle William had endowed Lafayette's chemistry professorship in 1865 (13). Hart's name was omitted from the corporate name because Lafayette College did not want the name of a faculty member to be attached to a company. Baker left that company in 1904 to form the J. T. Baker Chemical Company in Philipsburg, New Jersey to produce reagent grade chemicals. By the time of his death in 1935 the company listed 1,600 chemicals for sale in its catalog (31). This company is now a division of Tyco. Adamson remained with General Chemical and eventually became Director of Research at the company's headquarters in New York City. He served as a Lafayette trustee from 1920 until 1932 and died in Searsport, Maine on February 16, 1933 (33).

Porter William Shimer was the last to be awarded a Ph.D. degree in chemistry from Lafayette. Shimer was born in Shimersville, Pennsylvania on March 13, 1857. After graduation from Lafayette with an E.M. (mining engineer) degree in 1878, he was employed as chief chemist of the Thomas Iron Company for one year, then became Dr. Drown's chief assistant in his chemical laboratory, both at Lafayette, and later in his private laboratory, from 1879 until 1884. When Drown moved to the Massachusetts Institute of Technology in 1885, Shimer opened his own private chemical and metallurgical laboratory in Easton. From 1892 until 1902 he served as resident lecturer in iron and steel at Lafayette and also enrolled as a graduate student in 1898. He was awarded his Ph.D. in chemistry from Lafayette in 1899. In 1901 Shimer was awarded the John Scott Medal of the Franklin Institute for the invention of a platinum crucible with a water-cooled stopper, which greatly increased the speed and accuracy of the determination of carbon in the quantitative analysis of steel. He is also credited with the discovery of titanium carbide. He died December 7, 1938 (34, 35).

John Townsend Baker

Jenks Hall was replaced in 1902 with a new chemistry building, Gayley Hall. It was donated by James Gayley, an E.M. graduate of Lafayette's Class of 1876 and trustee of the college from 1892 until his death in 1920. Born in Lock Haven, Pennsylvania on October 11, 1855, Gayley was a scholarship student from a poor family. President William Cattell advised him that, because of his free tuition, he was under a moral obligation to return the money with interest if he was ever able to do so. Gayley eventually became Managing Director of Carnegie Steel in 1885 and then First Vice President of the U.S. Steel Corporation from 1901 until 1909. The building, 88 feet long and three stories tall, was constructed of brick and trimmed with limestone and terra-cotta at a cost of $34,000. Speakers at the dedication of the building included Thomas Drown, who by then was president of Lehigh University, Ira Remsen of Johns Hopkins University, and Dr. Henry Howe of Columbia University. Mr. Gayley received the Elliot

Cresson Medal of the Franklin Institute for the invention of the dry air blast process for the production of steel. He also won the Perkin Medal in 1913 and was a president of the American Institute of Mining Engineers (36, 37).

Students

Many early Lafayette graduates in chemistry headed west to seek their fortunes in the mining industry. One such individual who was especially successful in that career was Stuart Croasdale. Born in Delaware Water Gap, Pennsylvania on November 21, 1866, Croasdale earned a B.S. in chemistry in 1891 and a Ph.D. in 1898. He received what was probably the first post-doctoral fellowship in the history of the college from 1898 until 1891, then became the Chief Chemist at the Holden Lixiviation Company in Aspen, Colorado from 1891 through 1893. From 1894 through 1896 he worked as an assayer and chemist in Summitville and Gillett, Colorado and then became the chief chemist at the Globe Smelting and Refining Company in Denver from 1896 until 1900. In 1900 he became a consultant, selling his services to companies including Anaconda Copper and Calumet and Arizona Copper, and he eventually served as president of the Alma Gold Mining Company in Denver. Croasdale is best known as the co-inventor of the Pohle-Croasdale process for the treatment of refractory ores. He died in Denver on September 30, 1934 (38).

The Lafayette chemistry graduate who received the greatest variety of advanced degrees was probably George H. Meeker. Born in Philipsburg, New Jersey on August 13, 1871, Meeker graduated from Lafayette in 1893 with a B.S. in chemistry and remained there as a graduate student to earn an M.S. in 1895 and a Ph.D. in 1898. He was employed as Professor of Physics, Chemistry, Metallurgy, and Toxicology at the Medico-Chirurgical College in Philadelphia from 1897 through 1916 and Dean of the Department of Pharmaceutical Chemistry there from 1907 until 1916. While at that institution he earned a Pharm. D. in 1906 and a D.D.S. in 1907. From 1918 through 1941 he was the Dean of

the Medical School of the University of Pennsylvania. He received the L.L.D. from Ursinus College in 1905 and from Lafayette in 1925, and the Sc.D. from Villanova University in 1913 and from the University of Pennsylvania in 1940. Meeker, winner of the John Scott Medal of the Franklin Institute, was also an inventor of many mechanical, electrical, and chemical devices and an expert chemical and toxicological witness in many prominent court cases. He died in Hunt Lake, New Jersey on September 4, 1945 (39).

When Edward Hart retired in 1916, he was succeeded as William Adamson Professor and Head by Eugene C. Bingham. Bingham had earned a B.A. from Middlebury College in 1899 and a Ph.D. from Johns Hopkins University in 1905. He is best known as the founder of the modern science of rheology. Although he stepped down as department head in 1938, he remained at Lafayette as a research professor until 1945 (40, 42).

Near the end of Bingham's administration, Lafayette became the first chemistry department in the country to form a student affiliate chapter of the American Chemical Society. Students at Lafayette and nine other colleges had formed the Intercollegiate Student Chemists (ISC) in 1936, with a goal of forming a national organization and also strongly advocating the affiliation of students with the ACS. The ACS changed its national bylaws concerning associate members in 1936 in a way that allowed local sections to admit students to section membership. The Lehigh Valley Section quickly acted to change its local bylaws and suggested a series of resolutions allowing the formation of student affiliate chapters. These were submitted as a report to the Spring 1937 national meeting in Chapel Hill, NC. At the 1937 Fall National Meeting in Rochester NY, the ACS adopted bylaws for the establishment of student affiliate chapters. The students at Lafayette acted very quickly, passing a resolution at the first meeting of the Student Chemical Society in the fall of 1937 "to secure

the first chapter for Lafayette College." Charles Parsons, Secretary of the ACS, sent a letter to Dr. Crosen, the faculty advisor to the organization, that the application for affiliation was approved on November 15th, 1937 (41).

1938 - 1997

Bingham was succeeded as chemistry department head in 1938 by John H. Wilson, who had also come to Lafayette at the time of Edward Hart's retirement in 1916, but as the first Assistant Professor of Chemistry. He had earned his B.S. from Lafayette in 1905, then enrolled at Harvard University where he received an M.S. in 1907 and a Ph.D. in 1908. He was promoted to Associate Professor in 1919 and then to Professor in 1931. He headed the department from 1938 until his retirement in 1957 (40, 42, 43).

Wilson was replaced as department head by another Lafayette graduate (B.A., 1927), William F. Hart (no relation to Edward Hart). Hart earned an M.A. from Princeton University in 1928, then worked as an Instructor at Lafayette during the 1928-1929 school year. He left Lafayette to study at New York University, earning his Ph.D. there in 1936. He was rehired by Lafayette, holding the rank of Instructor from 1937 to 1939, Assistant Professor from 1939 to 1942, Associate Professor from 1942 to 1954, and finally Professor from 1954 until his retirement in 1971. He served as department head from 1957 until 1968 (42,44).

A major addition to chemistry at Lafayette during William Hart's tenure was the construction of the Olin Hall of Science. In 1955 the Olin Foundation donated $1.25 million for the construction of a 40,000 square foot engineering science building to house the physics, chemistry, graphics, and mathematics departments. Dedicated on January 11, 1957, it is still in use by the chemistry department (45,46).

Olin Hall of Science

William Hart was succeeded as department head in 1968 by Thomas G. Miller. Miller had earned his B.A. from Miami University in 1948, and his M.S. (1949) and Ph.D. (1951) degrees from the University of Illinois. He held the rank of Assistant Professor from 1957 to 1960, then Associate Professor from 1960 to 1969. He was promoted to Professor in 1969 and became the John D. and Francis H. Larkin Professor of Chemistry in 1974. Miller held that Chair until his retirement in 1987 (42, 46, 47).

Thomas Miller stepped down as head of the chemistry department in 1979. He was succeeded in that position by Laylin K. James, Jr., who had received his B.S. in 1950 and M.S. in 1952 from the University of Michigan, and his Ph.D. in 1958 from University of Illinois. He joined the Lafayette faculty as Assistant Professor in 1959 and was promoted to Associate Professor in 1966 and to Professor in 1977. He headed the department until 1984 and retired in 1990 (42, 46, 47).

James' successor as head of the chemistry was Joseph A. Sherma, Jr., who led the department from 1984 until 1997. Sherma received his B.S. from Upsala College in 1955 and his Ph.D. in analytical chemistry from Rutgers University in 1958. He served Lafayette as Instructor during the academic year 1958-1959, then was promoted to Assistant Professor in 1959, Associate Professor in 1963, and Professor in 1974. In 1982 he was named Charles A. Dana Professor of Chemistry, a title he held until 1991 when he was named the John D. and Francis H. Larkin Professor of Chemistry. Professor Sherma was the winner of the E. Emmet Reid Award of the Middle Atlantic Region of the American Chemical Society for Excellence in Teaching Chemistry in 1988 and the national ACS Award for Research at an Undergraduate College in 1995 (42, 46, 47).

The current head of the chemistry department since 1997 is H. David Husic. Professor Husic is a biochemist who received his B.S. from The Pennsylvania State University in 1977 and his Ph.D. from Michigan State University in 1982. He was hired by Lafayette as Assistant Professor in 1986 and promoted to Associate Professor in 1992 (48). A new 40,000 square foot facility for the chemistry and physics department, Charles Hugel Science Center, was completed in 2000. Attached to the Olin Hall of Science, it contains physical facilities that will allow Lafayette to remain the superb place to learn chemistry that it has been since the middle of the nineteenth century (46, 48).

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BOOK REVIEWS

A Philatelic Ramble through Chemistry. E. Heilbronner and F. A. Miller, VHCA, Verlag Helvetica Chemica Acta AG, Zürich, and WILEY-VCH GambH & Co. KGaA, Weinheim, 2004, ix + 268 pp, paper, ISBN 3-906390-31-4, $89.95.

There is something for everyone in this excellent book: the chemist, the historian of chemistry, and the philatelist. For the person like me, who is interested in all three areas, this book is the bible of chemical philately. This is the first book of its kind, a comprehensive review of how chemists and chemistry have been depicted on postage stamps and other philatelic items such as covers, souvenir sheets, and maximum cards. The authors, Edgar Heilbronner and Foil A. Miller, distinguished chemists and long-time philatelists, emphasize that the book is not a history of chemistry, since important parts of chemical history are missing for the simple reason that they have not found their way onto postage stamps. For example, at the time of printing, no postage stamps had been issued to honor Henry Cavendish, Joseph Black, Anders Ångström, Johann Balmer, Robert Bunsen, or Johannes Rydberg. Nonetheless, more than 1,000 stamps and other philatelic items are depicted.

This 268-page soft cover book, published in 2004, is identical in content to the hardcover version, which was published in 1998. Both were published jointly by Verlag Helvetica Chimica Acta of Switzerland and Wiley-VCH of the Federal Republic of Germany and printed in Germany. The printing and color reproduc-

tion of the philatelic material in the soft cover edition is superb, as it is in the hardcover edition. The new edition is welcomed, since the book is now more widely available compared with the limited edition hardcover version. The one drawback is the soft cover edition is about twenty-five percent smaller in size, making the notations and formula on some of the philatelic items difficult to read. The soft cover version has not been updated to include additional philatelic items of chemical interest issued since 1998.

Although each author was responsible for their individual chapters, their slightly different writing styles do not detract in any way from the readability of the book. Each thematic chapter starts with an overview of the discipline covered and follows with the chronological development of the discipline, using postage stamps and related philatelic material to illustrate the chemist or chemical topic discussed. For example, Chapter 1, entitled *The Beginnings,* contains a discussion of chemistry in Greece and the stamps illustrate the following: the elements that were known at the time; Pythagoras of Samos and his famous theorem; Democritos of Abdera who related the properties of substances to their shapes, and the classical four elements fire, air, water, and earth, as discussed by Aristotle and Plato. Chinese chemistry and alchemy are beautifully illustrated with stamps showing lacquer-ware; Chinese pottery; Tsai Lun, the inventor of paper; early papermaking; as well as fireworks and the Chinese invention of gunpowder. A beautiful souvenir sheet of six stamps issued by Gambia in 1993, each showing a different work of art, for example, illustrates Chinese pottery. A total of 44 philatelic items

illustrate this first chapter. An attempt has been made to place the text and the related illustrations on the same page. Thus it is visually easy to relate the illustration to the text, which is helpful in a book that includes many illustrations.

Chapter 2, entitled *Alchemy, the Chemistry of the Middle Ages*, includes a brief history of alchemy, which developed in Egypt and the Middle East, and independently in China and India. The stamps illustrate alchemists in literature and art as well as named alchemists who have appeared on stamps. The latter section includes stamps of Avicenna, a noted Persian physician; Albertus Magnus, a German scholar; Paracelsus, a Swiss physician and alchemist, Georgius Agricola, known as the 'father of mineralogy;' Robert Boyle, successful in transmuting alchemy into chemistry; and Joseph Priestley. There are many humorous anecdotes included in this highly readable and informative book: for example, the letter that Joseph Priestley wrote in 1777 to Benjamin Franklin indicating that he 'did not quite despair of finding the philosopher's stone,' to which Franklin is said to have replied that 'if he finds it, take care not to lose it again.'

The remainder of the book follows the same format, illustrating the fields of inorganic chemistry and the discovery of the elements, organic chemistry, physical and theoretical chemistry, spectroscopy, X-ray structure analysis, technical chemistry, and in the final chapter, miscellaneous topics.

One of the most enjoyable parts of the book I found to be "Chomical Errors on Chemical Stamps," part of Chapter 9, *Miscellaneous Topics*. The authors point out Yogi Berra's dictum 'You can observe a lot just by watching,' and illustrate their expertise in chemistry by pointing out numerous gaffes that have appeared on postage stamps and related items. The authors' first-prize worst chemical error on a stamp goes to the country of Monaco, for its 'inverted' methane molecule HC_4. An embarrassing blunder can be found on a stamp issued by France in honor of Henri Moisson, who received the Nobel Prize for the discovery of fluorine. The stamp shows the reaction of hydrogen and fluorine to produce hydrogen fluoride, whereas the opposite reaction was intended to represent the discovery. The 'Golden Turkey' award for 'Mad Benzene Rings on Stamps' goes to a stamp issued in 1971 by Argentina. Instead of benzene we are offered the 'hexacarbenobenzene' molecule $C_6(CH)_6$. Wrong names and dates are numerous on stamps of a scientific nature. A 1977 stamp from the Comoro Islands purports to show five Nobel Prize laureates in chemistry, but both Banting and Hench received the prize in medicine and Perrin got his for physics. In addition, Madame Curie got her chemistry prize in 1911 instead of 1913 as indicated. Being able to catch these and numerous other errors on stamps reflects the expertise of both authors in their field.

As one who is interested in postal history, I was particularly fascinated with the excellent array of covers displayed throughout the book. Many of these covers, borrowed from private collections, were autographed by famous chemists, and many had gone through the mails, and hence included a dated cancellation, which commemorated some historical event in the history of chemistry. One cover, for example, was a first-day cover from Sweden with an early stamp honoring Nobel and signed by members of the 1994 Chemistry Nobel committee. Another interesting cover, commemorating the centenary in 1971 of the birth of Victor Grignard, was addressed to Professor Vladimir Prelog, who went on to win the Nobel in chemistry in 1975. The discovery of crown ethers seems to have been anticipated by a cancel on a 1960 cover, which shows the formula of a cyclic polyformaldehyde molecule consisting of six formaldehyde units. The cover is autographed by Jean-Marie Pierre Lehn and Donald Cram, who shared the Nobel Prize in 1987 with Charles Pedersen.

The book is loaded with interesting facts, each illustrated with a stamp or related material. For example, the authors illustrate maximum card (a post card illustrated with the same image as the postage stamp affixed), showing a mandarin-duck-shaped lacquer box dated 433 B.C. and to explain how lacquer works as it does. This reviewer was not aware that Isaac Newton, depicted on numerous stamps, devoted thirty years to the study of alchemy, beginning in the mid 1660s; or that Dmitri Mendeleev, depicted on a 1969 Russian stamp, was the youngest of seventeen children and created his periodic system in one day. Another interesting fact is that the early aniline dyes, the first of which was discovered by William Henry Perkin in 1856, were dear to philatelists because they were used for printing later versions (of different denominations and color) of the first stamp ever issued, the British 'Penny Black.'

The authors' efforts to document all text and the numerous illustrations are to be commended and make the book a particularly good reference for both chemical philately and the history of chemistry. For example, Chapter 5**,** *Physical and Theoretical Chemistry*, includes 69 references and the history is illustrated by 166 stamps and related material. Chapter 4, *Organic Chemistry*,

takes the prize for the largest number of illustrations, with 218 items. Although not mentioned by the authors, it becomes clear on reading the book that the United States has not done a particularly good job in documenting its chemical heritage philatelically. This is not to say that chemists have never been depicted on stamps of the U. S. Joseph Priestley, Percy Julian, and George Washington Carver have been so honored. However, to date, no American Nobel Prize winner in chemistry has appeared on a U. S. postage stamp.   To make matters worse, other countries have so honored American chemists, for example John H. Northrop on a stamp from Gabon, Linus Pauling on a stamp from Upper Volta, and Glenn Seaborg on a stamp from Malagasy. Great Britain and Sweden have done a particularly good job in depicting their chemical heritage and particularly the Noble Prize with postage stamps and related material.

Another strength of the book, especially to the chemical philatelist, is the excellent stamp identifica-

tion list at the end of the book. For each illustration in the entire book, the number, country, date of issue, the denomination, the Scott number, and the subject matter are clearly itemized by chapter. It is unfortunate that publishers other than Scott (the United States) were unwilling to have their numbers used in combination with those of another system, since excellent catalogs exist such as Gibbons, Michel, and Yvert.

In conclusion, this book has served its purpose in documenting, in the highest quality, our chemical heritage as depicted on philatelic material.   Although the title of the book only refers to chemistry, there is much included to interest the physicist, and rightfully so because of its impact on chemistry. The chapters on spectroscopy and X-ray structure analysis are particularly good examples of this. There is much here for the scientist and the nonscientist who is interested in chemistry, and the book is a thoroughly enjoyable read. *John B. Sharkey, Pace University, New York, NY 10038.*

Gay-Lussac: Scientist and Bourgeois. Maurice Crosland, Cambridge University Press, New York and Cambridge, 1978; new paperback edition 2000, xvi + 262 pp; appendix, notes and bibliography.

Cambridge University Press has done the history of science community a fine service by republishing in paperback Maurice Crosland's landmark biography of Joseph Louis Gay-Lussac (1778-1850), which has long been out of print. As historians of chemistry well know, Gay-Lussac's significance extends far beyond the establishment of his eponymous law of combining gas volumes (1809)—although that discovery alone would have been sufficient to immortalize his name. A provincial student educated at the Ecole Polytechnique in Paris soon after its founding, Gay-Lussac became assistant to Berthollet, quickly proving his brilliance in precise physical and chemical research, particularly in volumetric studies of gases. Elected to the Académie des Sciences at the extraordinary age of 28, he was appointed to simultaneous professorships in the Paris Faculty of

Science (the Sorbonne) and the Ecole Polytechnique; in 1832 he gave up the former post to accept a position at the Muséum d'Histoire Naturelle. By the 1830s these posts, as well as additional lucrative bureaucratic and consulting work, made Gay-Lussac both very wealthy and politically influential.

In the first decade of the century, Gay-Lussac had been a member of the Société d'Arcueil, the informal group of young chemists and physicists around Berthollet and Laplace. No one in history, except perhaps Robert Bunsen in the next generation, could compare to the precision and artistry with which Gay-Lussac handled and studied gases, but he was also a superb "wet" chemist, as well. Together with his friend L. J. Thenard, he virtually controlled Parisian academic chemistry in the 1820s and 1830s, before he became sidetracked by consulting and government work. He was also one of the most brilliant teachers of the century, his mentorship of the young Justus Liebig being the most obvious example.

Crosland's biography is not only one of the best scientific biographies of the last generation, it is also one of the earliest modern monographic biographies of an important nineteenth-century French chemist. Using an extraordinary range of the sources, including masses of surviving letters and other manuscripts, Crosland builds a compelling picture of Gay-Lussac's life, both in scientific and personal terms. One of the great

strengths of the work is its analysis of the political and social context of science in Restoration and Orleanist France. It is also beautifully written, providing an appealing account of Gay-Lussac's attractive personality. All in all, the book marks a milestone that has lost none of its significance twenty-six years after its first appearance in print. *Alan J. Rocke, Department of History, Case Western Reserve University.*

DuPont: From the Banks of the Brandywine to Miracles of Science. Adrian Kinnane, Johns Hopkins University Press, Baltimore, MD, 2002, distributed for the DuPont Co., 272 pp, 598 illustrations, ISBN 0-8018-7059-3, $29.95.

This 11" x 11" 4-lb. coffee-table book was commissioned by DuPont on the occasion of its 200th birthday. The author is affiliated with History Associates Inc, which also provided research and editing services from several other staff members. The photographs are largely from the collection of Hagley Museum and Library. Although DuPont's founding and early development have been the subject of earlier accounts, historians of chemistry will find the first six chapters of primary interest. The more recent history of the company covering the last three decades is detailed for the first time in this book.

In Chapter 1, "A Vision and Product," the author presents the fairly familiar story but with an eye to detail of the founding of the US company by Eleuthère Irénée du Pont (E. I.), who visualized its successful future in the manufacture of gun powder. The original powder works on the Brandywine River near Wilmington, DE, were called "Eleuthère Mills." Considerable detail is presented about the financing and operation in the early days and of the frustrations and challenges E. I. faced up to his death in 1834. After a three-year transition in management, Alfred, one of E. I.'s sons, took over the company. He was succeeded in 1850 by another son Henry, a graduate of West Point.

The transformation of the growing company from the Civil War to the end of the 19th century is covered

in Chapter 2, "Family Firm, Growing Nation." The reader is informed about expansion of products to include guncotton ("smokeless powder") and dynamite; but we also learn about the du Pont family: those who distinguished themselves by service in the Civil War, a diarist daughter of E.I., marriages, births, and personal tragedies.

Chapter 3, "The 'Big Company,'" covers continued expansion and diversity of DuPont, partially prompted by the demands of World War I. By 1919 the company's assets had skyrocketed, and new directions were sought. The investment into General Motors and development of new product lines such as dyestuffs, plastics, and paint are described in Chapter 4, "Serving the New Customer." The company was organized into departments; the Buffalo plant was opened for production of rayon and cellophane; and DuPont began supplying the auto and film industries.

Charles Stine is credited with the vision for developing a solid commitment to basic research in the 1920s, as we learn in Chapter 5, "Discovery." He called investment into research "patient money," whose dividends might not materialize for a long time. Once the executives were convinced, DuPont went forward with an aggressive program of basic investigations in five areas—catalysis, colloids, polymerization, chemical engineering, and chemical synthesis—each headed by a distinguished research chemist. Indeed, in that 'golden era' of discovery, DuPont came forth with highly successful products such as neoprene and nylon. It was in 1935 when, under severe public criticism for its undue profiteering at the expense of the public, DuPont coined the famous—now, in some minds, politically incorrect—motto, "Better Things for Better Living..Through Chemistry."

The era of World War II, covered in Chapter 6, "Science and the Affluent Society," provided the challenge of contributing to the war effort, which DuPont did under the supervision of Crawford H. Greenewalt, who later headed the company. DuPont collaborated in construction of the nuclear reactor at Oak Ridge as part of the Manhattan Project, with the understanding that the company would be remunerated in the amount of $1 above the cost. (In the final settlement, the government auditors insisted DuPont return 33 cents because the war ended before their contract did.) At the end of the war, Greenewalt oversaw the adjustment to peacetime manufacturing and the appearance of products such as Dacron®, Orlon®, and Teflon®.

The more recent evolution of DuPont, described in detail in Chapters 7-9, includes the prosperity of the 1960s superimposed on social and economic pressures brought on by concerns for the environment; the inevitable tension between basic and applied research; new directions toward pharmaceuticals, agricultural chemistry, and biotechnology; discontinuation of the manufacture of explosives in the 1970s; and response to the energy crisis.

Although the book clearly sends a message of pride in the DuPont Company, it is presented in a highly objective style and enriched with myriad photographs and reproductions of archival documents, aside from the promotional materials (The reader is told that the dust cover is made of Tyvek® and given a web site for further information.)   In this reviewer's opinion, the author has effectively presented a detailed, honest account of the founding, growth, and evolution of DuPont. It includes not only the major successes but also misjudgments, financial failures, and family squabbles. The ample Endnotes for each chapter are particularly appreciated by the historian. Especially helpful for an overview of DuPont's hierarchy is a partial "family tree" on p 9, depicting members of the du Pont family (and spouses) who have played a role in the company's founding and management. It would have been even more useful had it included dates of service. The index appears to be extensive and accurate. The book will be attractive on the coffee table, but it is far more than a decoration—a source book of a chapter in the history of American industry. *Paul R. Jones, University of Michigan*

The Last Alchemist: Count Cagliostro, Master of Magic in the Age of Reason. Iain McCalman, HarperCollins, New York, 2003, xii + 246 pp, ISBN 0-06-000690-0, $25.95.

Giuseppe Balsamo, alias Count Alessandro di Cagliostro, among several other pseudonyms (1743-1795) gained fame and infamy in France, Russia, and England in the latter half of the 18th century for his reputed skills in alchemy, mysticism, and necromancy. Yet his names are far less familiar than those of his alchemical predecessors of the previous century or his contemporaries with more formal education than he possessed. He warrants no mention in the chemical histories of Partington or Ihde, and an internet search under "cagliostro" yields only four hits, provided by *Theosophy*, *Encyclopedia Britannica,* Google, and Alpha Chi

Sigma. Author McCalman, Director of the Humanities Research Centre, Australian National University, provides a highly readable rendition of the man, warts and all. We are told how the author was motivated to write this account in the very last paragraph of the book:

> Of all the real and mythic lives of Giuseppe Balsamo—Alessandro Cagliostro, the one, finally, that attracts me most is the one I encountered first outside the house of Balsamo in Palermo—the one that launched my project of writing this book.

In stating this, McCalman has chosen to accept some "facts" of Cagliostro's life over others, for the account of this character in the *Theosophy* source indicates mystery and uncertainty about the location of his birth. The sources for this book are numerous, however, including archival material from libraries in Australia, Paris, Strasbourg, London, Oxford, Italy, Basel, and California. The reader is reassured that many of the letters,

statements, and sometimes gory details are based upon original documents, listed at the end as Notes. These have been examined with the help of several translators. The result is a hybrid between a scholarly biography and an historical novel that is revealing and informative, yet presented by means of an amusing and palatable narrative.

We are taken on a journey of this controversial but incredibly resourceful character from birth to death. The prologue, chapter headings, and epilogue reveal the course of that journey: House of Balsamo, Freemason, Necromancer, Shaman, Copt, Prophet, Rejuvenator, Heretic, Immortal. On the way we learn of Cagliostro's direct encounters with individuals in high stations in several countries, many of whom had direct access to kings, queens, cardinals, and the pope. Essentially self taught, he is reputed to have carried out alchemical trans-

formations, cured the sick, predicted coming events, and communed with the dead. To call him simply an "alchemist" understates his reputation. As a dedicated Freemason, he made contacts with other initiates wherever he traveled, along with his long suffering but conniving wife Lorenza Seraphina Feliciani, whom he married when she was 14. It was eventually she who was responsible for his terminal imprisonment in Italy, after she reported his active role in Freemasonry, a crime in the eyes of the Roman Catholic Church.

A reader acquires a very tangible sense of the way in which the Count and Countess seized every conceivable opportunity to gain fame and fortune in clever, albeit often unscrupulous ways, thanks to McCalman's ability to weave archival "facts" into a smooth, lively narrative. *Paul R. Jones, University of Michigan.*

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