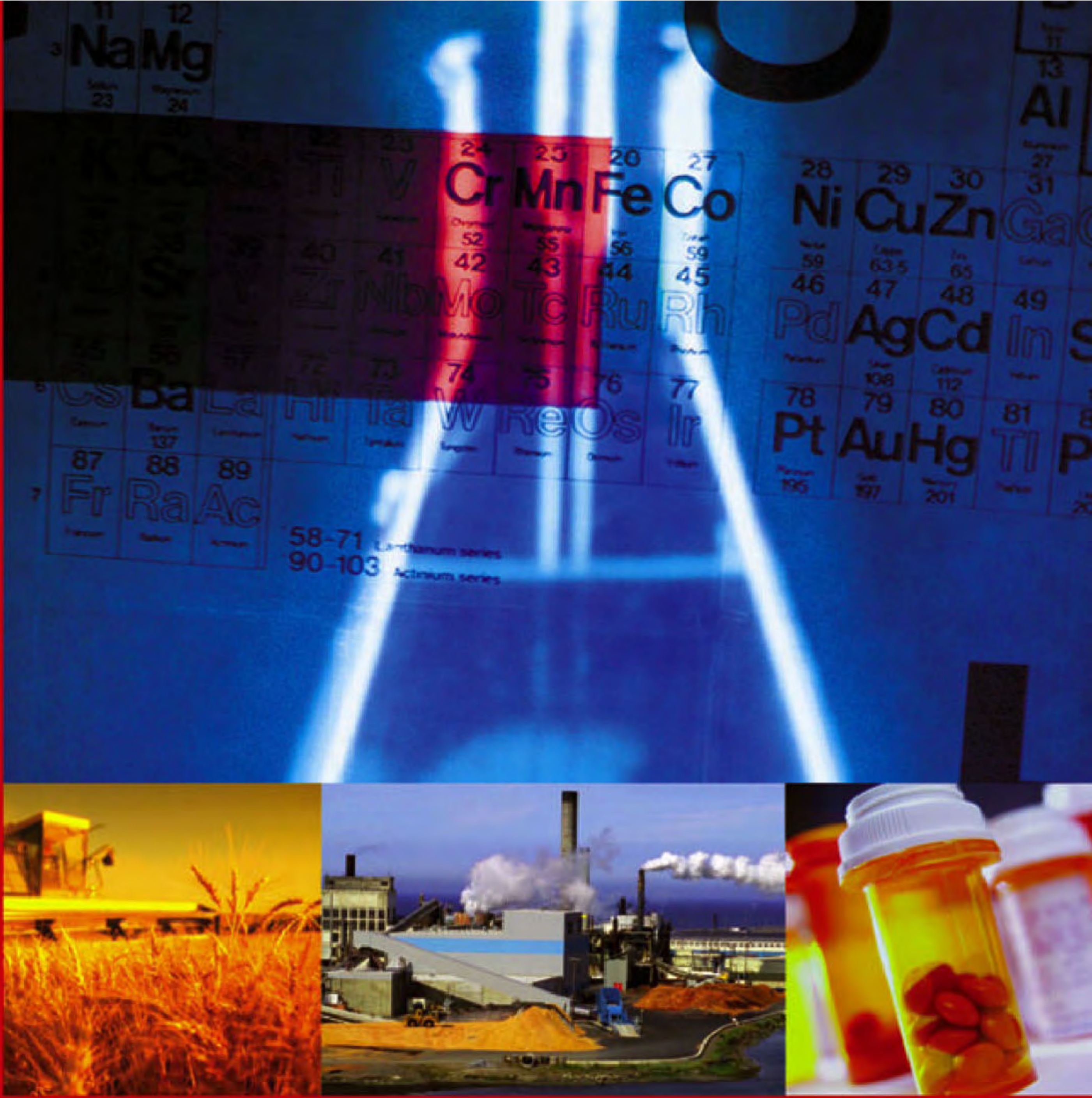

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Chemistry: Foundations and Applications

J. J. Lagowski, Editor in Chief

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Preface

Chemistry. The word conjures up mystery—perhaps magic—smoke, fireworks, explosions, unpleasant odors. But it could evoke "smokeless burning," which would be invisible, fluorescent lights, "neon" signs, the quiet crumbling of rocks under the pressure of freezing water, the slow and quiet formation of caves in limestone, and the delightful scents of perfumes or fruit aromas. There is no magic, only knowledge and understanding. We offer this *Encyclopedia* as a contribution to help readers gain knowledge and understanding of chemistry.

Chemistry was manifested as an art at the beginnings of civilization. The early decorative chemical arts included the preparation of pigments such as the Egyptian blue applied to King Tutankhamen's golden death mask; the various bronze alloys that were used to make vases in the ancient world of the Middle East as well as in China; and the glass objects that have been found in Mesopotamia (now known as Iraq). Those chemical arts became a science in the eighteenth century when Antoine Laurent Lavoisier (1743–1794) led what has been called "the chemical revolution." Using accurate measurements of primarily mass, early chemists began to make order out of the myriad of substances that are found in the natural world. This order was eventually expressed in a number of chemical concepts that include the laws of chemical composition (constant composition, mass conservation, multiple proportions), periodicity, the nature of atoms, chemical bonding, and a variety of concepts involving chemical structures. The early symbiosis of chemistry with civilization remains. Chemistry is still a useful science in the advancement of civilization. Chemists have developed and refined the core concepts of chemistry to the point where they have become powerful tools to assist humankind in the acquisition of materials of practical use to extend and preserve civilization. Humans now have available a broader array of substances with a remarkable spectrum of properties than was available before chemistry became a science. Light emitting diodes (LEDs) produce more light than the individual torches, candles, and oil lamps of the distant past—indeed, than the incandescent light bulbs of the immediate past—more efficiently and with less pollution. Polymeric materials or composites can be produced with virtually any property desired—from stretching clingy Saran Wrap to Kevlar used in bullet proof vests; from nonstick Teflon to optical fibers; from rubber objects that are impervious to oil and gasoline to tires that can be used for 100,000 miles before needing replacement; from fibers that compete with (in some cases surpass) natural materials to plastics that have more desirable optical properties than glass. In a word, chemistry is *everywhere*.

There is no magic, only knowledge and understanding.

These volumes are a contribution to assist readers in their understanding of chemistry and chemical ideas and concepts. The 509 articles have been carefully chosen to provide basic information on a broad range of topics. For those readers who desire to expand their knowledge of a topic, we have included bibliographic references to readily accessible sources.

The continual evolution of the discipline of chemistry is reflected in our treatment of the elements. The careful reader will note that we have included articles for the first 104 elements; the remainder of the elements are "recently" discovered or exist only as short-lived species and, accordingly, are not readily available for the usual chemical studies that reveal, for example, their bulk properties or reactivity and much of the "standard chemistry" that is of interest. Much of what little we know about the elements beyond 104 permits us to place these elements in their appropriate places in the periodic table, which nevertheless still turns out to be quite insightful from a chemical point of view.

Entries in the *Encyclopedia* are in alphabetic sequence. Cross-references appear in small capitals at the ends of the articles to help readers locate related discussions. Articles range from brief, but concise, definitions to extensive overviews that treat key concepts in larger contexts. A list of common abbreviations and symbols, and a list of the known elements, as well as a modern version of the periodic table are included in the For Your Reference section at the beginning of each volume. A glossary and a comprehensive index appear at the end of each volume. Contributors are listed alphabetically, together with their academic and professional affiliations, at the beginning of each volume.

Following this preface, we offer a topical arrangement of the articles in the *Encyclopedia*. This outline provides a general overview of the principal parts of the subject of chemistry and is arranged in alphabetical order.

Many individuals have contributed greatly and in many ways to this *Encyclopedia*. The associate editors—Alton J. Banks, Thomas Holme, Doris Kolb, and Herbert Silber—carried the major responsibility in shaping the intellectual content of the *Encyclopedia*. The authors of the articles executed that plan admirably and we thank them for that effort.

The staff at Macmillan Reference USA—Marie-Claire Antoine, Hélène Potter, Ray Abruzzi, Gloria Lam, and Christine Slovey—have been outstanding in their dedication and contributions to bring this *Encyclopedia* from its initial concept to the current reality. Without their considerable input, insightful guidance, and effort this *Encyclopedia* would never have seen the light of day. I take this opportunity to thank them personally and publicly. I am particularly grateful to Rita Wilkinson, my administrative assistant for her persistent and careful attention to details that kept the editorial office and my office connected for the smooth transmission of numerous critical details. I am especially grateful to Christine Slovey who, through her determined efforts and dedication, made a potentially difficult and tedious task far less onerous and, indeed, enjoyable.

J. J. Lagowski

Topical Outline

Analytical Chemistry Applications

Adhesives
Agricultural Chemistry
Analytical Chemistry
Bleaches
Ceramics
Chemical Engineering
Chemical Informatics
Coal
Cosmetics
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Detergents
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Astrochemistry

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For Your Reference

TABLE 1. SELECTED METRIC CONVERSIONS

WHEN YOU KNOW	MULTIPLY BY	TO FIND
Temperature		
Celsius (˚C)	1.8 (˚C) +32	Fahrenheit (˚F)
Celsius (˚C)	˚C +273.15	Kelvin (K)
degree change (Celsius)	1.8	degree change (Fahrenheit)
Fahrenheit (˚F)	[(˚F) −32] / 1.8	Celsius (˚C)
Fahrenheit (˚F)	[(˚F −32) / 1.8] +273.15	Kelvin (K)
Kelvin (K)	K −273.15	Celsius (˚C)
Kelvin (K)	1.8(K −273.15) +32	Fahrenheit (˚F)

WHEN YOU KNOW	MULTIPLY BY	TO FIND
Distance/Length		
centimeters	0.3937	inches
kilometers	0.6214	miles
meters	3.281	feet
meters	39.37	inches
meters	0.0006214	miles
microns	0.000001	meters
millimeters	0.03937	inches

WHEN YOU KNOW	MULTIPLY BY	TO FIND
Capacity/Volume		
cubic kilometers	0.2399	cubic miles
cubic meters	35.31	cubic feet
cubic meters	1.308	cubic yards
cubic meters	8.107×10^{-4}	acre-feet
liters	0.2642	gallons
liters	33.81	fluid ounces

WHEN YOU KNOW	MULTIPLY BY	TO FIND
Area		
hectares (10,000 square meters)	2.471	acres
hectares (10,000 square meters)	107,600	square feet
square meters	10.76	square feet
square kilometers	247.1	acres
square kilometers	0.3861	square miles

WHEN YOU KNOW	MULTIPLY BY	TO FIND
Weight/Mass		
kilograms	2.205	pounds
metric tons	2205	pounds
micrograms (μg)	10^{-6}	grams
milligrams (mg)	10^{-3}	grams
nanograms (ng)	10^{-9}	grams

TABLE 2. ALPHABETIC TABLE OF THE ELEMENTS

Symbol	Element	Atomic Number	Atomic Mass*	Symbol	Element	Atomic Number	Atomic Mass*
Ac	Actinium	89	(227)	Mt	Meitnerium	109	(266)
Al	Aluminum	13	26.982	Md	Mendelevium	101	(258)
Am	Americium	95	(243)	Hg	Mercury	80	200.59
Sb	Antimony	51	121.75	Mo	Molybdenum	42	95.94
Ar	Argon	18	39.948	Nd	Neodymium	60	144.24
As	Arsenic	33	74.922	Ne	Neon	10	20.180
At	Astatine	85	(210)	Np	Neptunium	93	237.048
Ba	Barium	56	137.33	Ni	Nickel	28	58.69
Bk	Berkelium	97	(247)	Nb	Niobium	41	92.908
Be	Beryllium	4	9.012	N	Nitrogen	7	14.007
Bi	Bismuth	83	208.980	No	Nobelium	102	(259)
Bh	Bohrium	107	(262)	Os	Osmium	76	190.2
B	Boron	5	10.811	O	Oxygen	8	15.999
Br	Bromine	35	79.904	Pd	Palladium	46	106.42
Cd	Cadmium	48	112.411	P	Phosphorus	15	30.974
Ca	Calcium	20	40.08	Pt	Platinum	78	195.08
Cf	Californium	98	(251)	Pu	Plutonium	94	(244)
C	Carbon	6	12.011	Po	Polonium	84	(209)
Ce	Cerium	58	140.115	K	Potassium	19	39.1
Cs	Cesium	55	132.90	Pr	Praseodymium	59	140.908
Cl	Chlorine	17	35.453	Pm	Promethium	61	(145)
Cr	Chromium	24	51.996	Pa	Protactinium	91	231.036
Co	Cobalt	27	58.933	Ra	Radium	88	226.025
Cu	Copper	29	63.546	Rn	Radon	86	(222)
Cm	Curium	96	(247)	Re	Rhenium	75	186.207
Ds	Darmastadtium	110	(269)	Rh	Rhodium	45	102.906
Db	Dubnium	105	(262)	Rb	Rubidium	37	85.47
Dy	Dysprosium	66	162.50	Ru	Ruthenium	44	101.07
Es	Einsteinium	99	(252)	Rf	Rutherfordium	104	(261)
Er	Erbium	68	167.26	Sm	Samarium	62	150.36
Eu	Europium	63	151.965	Sc	Scandium	21	44.966
Fm	Fermium	100	(257)	Sg	Seaborgium	106	(263)
F	Fluorine	9	18.998	Se	Selenium	34	78.96
Fr	Francium	87	(223)	Si	Silicon	14	28.086
Gd	Gadolinium	64	157.25	Ag	Silver	47	107.868
Ga	Gallium	31	69.723	Na	Sodium	11	22.990
Ge	Germanium	32	72.61	Sr	Strontium	38	87.62
Au	Gold	79	196.967	S	Sulfur	16	32.066
Hf	Hafnium	72	178.49	Ta	Tantalum	73	180.948
Hs	Hassium	108	(265)	Tc	Technetium	43	(98)
He	Helium	2	4.003	Te	Tellurium	52	127.60
Ho	Holmium	67	164.93	Tb	Terbium	65	158.925
H	Hydrogen	1	1.008	Tl	Thallium	81	204.383
In	Indium	49	114.82	Th	Thorium	90	232.038
I	Iodine	53	126.905	Tm	Thulium	69	168.934
Ir	Iridium	77	192.22	Sn	Tin	50	118.71
Fe	Iron	26	55.847	Ti	Titanium	22	47.88
Kr	Krypton	36	83.80	W	Tungsten	74	183.85
La	Lanthanum	57	138.906	U	Uranium	92	238.029
Lr	Lawrencium	103	(260)	V	Vanadium	23	50.942
Pb	Lead	82	207.2	Xe	Xenon	54	131.29
Li	Lithium	3	6.941	Yb	Ytterbium	70	173.04
Lu	Lutetium	71	174.967	Y	Yttrium	39	88.906
Mg	Magnesium	12	24.305	Zn	Zinc	30	65.38
Mn	Manganese	25	54.938	Zr	Zirconium	40	91.224

*Atomic masses are based on the relative atomic mass of ^{12}C=12. These values apply to the elements as they exist in materials of terrestrial origin and to certain artificial elements. Values in parenthesis are the mass number of the isotope of the longest half-life.

TABLE 3. COMMON ABBREVIATIONS, SYMBOLS, AND ACRONYMS

’	minute (of arc); single prime
”	second (of arc); double prime
+	plus
$^{+}$	positive charge
−	minus
$^{-}$	negative charge
±	plus-or-minus
∓	minus-or-plus
×	multiplied by
·	multiplied by
÷	divided by
=	equals
≠	not equal to
∽	about, approximately
≅	congruent to; approximately equal to
≈	approximately equal to
≡	identical to; equivalent to
<	less than
≤	less than or equal to
>	greater than
≥	greater than or equal to
%	percent
°	degree (temperature; angle of arc)
@	at
—	single bond
═	double bond
: :	double bond
≡	triple bond
: : :	triple bond
∞	infinity
∝	variation
∂	partial derivative or differential
α	proportional to, alpha
√	square root
Δ	delta; increment of a variable
ϵ_0	dielectric constant; permittivity
θ	plane angle
λ	wavelength
μ	magnetic moment; micro
μA	microampere
μC	microcoulomb
μF	microfarad
μg	microgram
μg/ml	microgram per milliliter
μK	microkelvin
μm	micrometer (also called micron)
μmol;	micromole
μs, μsec	microsecond
ν	frequency
υ	velocity
π or pi	ratio of the circumference of a circle to its diameter; double as in double bond
σ	single as in single bond; Stefan-Boltzmann constant
Σ	summation
ϕ	null set
ψ	amplitude of a wave (as in *wave,* or *psi, function)*
→	reaction to right
←	reaction to left
↔	connecting resonance forms
⇆	equilibrium reaction beginning at right
⇄	equilibrium reaction beginning at left
⇌	reversible reaction beginning at left
⇋	reversible reaction beginning at right
↑	elimination
⇓	absorption
a	acceleration
A	area
a_o	Bohr Unit
AAS	atomic absorption spectroscopy
ABS	alkylbenzene sulfate
ACS	American Chemical Society
ADH	alcohol dehydrogenase
ADP	adenosine diphosphate
AEC	Atomic Energy Commission
AES	atomic emission spectroscopy
AFM	atomic force microscope; atomic force microscopy
AFS	atomic fluorescence spectroscopy
ALDH	aldehyde dehydronase
amp	ampere
AMS	accelerator mass spectrometry
AMU	atomic mass unit
atm.	standard atmosphere (unit of pressure)
ATP	adenosine triphosphate
β	beta
b.p.	boiling point
Btu	British thermal unit
c	centi-; speed of light
C	carbon; Celsius; centigrade; coulomb
C	heat capacity; electric capacitance

TABLE 3. COMMON ABBREVIATIONS, SYMBOLS, AND ACRONYMS [continued]

Ci	Curies
cm	centimeter
CT	computed tomography
d	d-orbital
D	dipole moment
DC	direct current
deg	degree
dr	diastereomer ratio
e	elementary charge
E	electric field strength; energy
E_a	activation energy
E_g	bandgap energy
EA	electron affinity
er	enantiomer ratio
eV	electron volts
f	f-orbital
F	Fahrenheit; Faraday's constant; fluorine
F	force
g	gram
g	g-orbital; gas
h	hour
h	Planck's constant
Hz	hertz
i	i-orbital
IUPAC	International Union of Pure and Applied Chemistry
J	joule
J	electric current density
k	k-orbital
K	degrees Kelvin; Kelvin; potassium
K_a	acidity constant for the dissociation of weak acid (the weaker the acid, the lower the K_a value
k_B	Boltzmann's constant
Kg	kilogram
kHz	kilohertz
kJ	kilojoule
kJ mol	kilojoule mole
km	kilometer
K_m	Michaelis constant
l	length; liquid
L	lambert; liter
L	length; Avogadro's constant
LD	lethal dose
L/mole	liters per mole
ln	natural logarithm
log	logarithm
m	meter; milli-; molal (concentration)
m	mass
M	molar (concentration)
m_e	electron mass
mA	milliamperes
mg	milligram
mg/L	milligrams per liter
MHz	megahertz
min	minute
ml	milliliter
MO	molecular orbital
p	p-orbital
ω	omega
ppb	parts per billion
ppm	parts per million
ppt	parts per trillion
psi	per square inch; English for ψ
q	quantity
REM	Roentgen Equivalent Man (radiation-dose unit of measure)
s	solid; s-orbital
S	entropy
sec	second; secant
SEM	scanning electron microscope
SI	Système Internationale (International System of Measurements)
SPM	scanning probe microscope
STM	scanning tunneling microscope
STP	standard temperature and pressue (˚C, 1 atm)
Sv	sievert unit (1 Sv = 100 REM; used to measure radiation dose)
t	time
T	moment of force, thermodynamic temperature (in degrees Kelvin); torque
T_c	critical temperature
TEM	transmission electron microscope
u	unified atomic mass unit
U	electric potential
V	electric potential; vanadium; volume
V	volt
vap.	vaporization
VB	valence bond
vel.	velocity
VSEPR	valence shell electron pair repulsion
Z	atomic number

PERIODIC TABLE OF THE ELEMENTS*†

	I	II													III	IV	V	VI	VII	VIII
																				2 HELIUM **He** 4.003
5	3 LITHIUM **Li** 6.941	4 BERYLLIUM **Be** 9.012												p	5 BORON **B** 10.811	6 CARBOM **C** 12.011	7 NITROGEN **N** 14.007	8 OXYGEN **O** 15.999	9 FLUORINE **F** 18.998	10 NEON **Ne** 20.180
	11 SODIUM **Na** 22.990	12 MAGNESIUM **Mg** 24.305						1 HYDROGEN **H** 1.008							13 ALUMINUM **Al** 26.982	14 SILICON **Si** 28.086	15 PHOSPHORIUS **P** 30.974	16 SULFUR **S** 32.066	17 CHLORINE **Cl** 35.453	18 ARGON **Ar** 39.948
	19 POTASSIUM **K** 39.1	20 CALCIUM **Ca** 40.08	d	21 SCANDIUM **Sc** 44.966	22 TITANIUM **Ti** 47.88	23 VANADIUM **V** 50.942	24 CHROMIUM **Cr** 51.996	25 MANGANESE **Mn** 54.938	26 IRON **Fe** 55.847	27 COBALT **Co** 58.933	28 NICKEL **Ni** 58.69	29 COPPER **Cu** 63.546	30 ZINC **Zn** 65.38		31 GALLIUM **Ga** 69.73	32 GERMANIUM **Ge** 72.61	33 ARSENIC **As** 74.922	34 SELENIUM **Se** 78.96	35 BROMINE **Br** 79.904	36 KRYPTON **Kr** 83.80
	37 RUBIDIUM **Rb** 85.47	38 STRONTIUM **Sr** 87.62		39 YTTRIUM **Y** 88.906	40 ZIRCONIUM **Zr** 91.224	41 NIOBIUM **Nb** 92.908	42 MOLYBDENIUM **Mo** 95.94	43 TECHNETIUM **Tc** (98)	44 RUTHENIUM **Ru** 101.07	45 RHODIUM **Rh** 102.906	46 PALLADIUM **Pd** 106.42	47 SILVER **Ag** 107.868	48 CADMIUM **Cd** 112.411		49 INDIUM **In** 114.82	50 TIN **Sn** 118.71	51 ANTIMONY **Sb** 121.75	52 TELLURIUM **Te** 127.60	53 IODINE **I** 126.905	54 XENON **Xe** 131.29
	55 CESIUM **Cs** 132.90	56 BARIUM **Ba** 137.33		71 LUTETIUM **Lu** 174.967	72 HAFNIUM **Hf** 178.49	73 TANTALUM **Ta** 180.948	74 TUNGSTEN **W** 183.85	75 RHENIUM **Re** 186.207	76 OSMIUM **Os** 190.2	77 IRIDIUM **Ir** 192.22	78 PLATINUM **Pt** 195.08	79 GOLD **Au** 196.967	80 MERCURY **Hg** 200.59		81 THALLIUM **Tl** 204.383	82 LEAD **Pb** 207.2	83 BISMUTH **Bi** 208.980	84 POLONIUM **Po** (209)	85 ASTATINE **At** (210)	86 RADON **Rn** (222)
	87 FRANCIUM **Fr** (223)	88 RADIUM **Ra** 226.025		103 LAWRENCIUM **Lr** (260)	104 RUTHERFORDIUM **Rf** (261)	105 DUBNIUM **Db** (262)	106 SEABORGIUM **Sg** (263)	107 BOHRIUM **Bh** (262)	108 HASSIUM **Hs** (265)	109 MEITNERIUM **Mt** (266)	110 DARMASTADTIUM **Ds** (269)	111 UNUNUNIUM **Uuu** (272)	112 (?)							

f	57 LANTHANUM **La** 138.906	58 CERIUM **Ce** 140.15	59 PRAESEODYMIUM **Pr** 140.908	60 NEODYMIUM **Nd** 144.24	61 NEODYMIUM **Pm** (145)	62 SAMARIUM **Sm** 150.36	63 EUROPIUM **Eu** 151.965	64 GADOLINIUM **Gd** 157.25	65 TERBIUM **Tb** 158.925	66 DYSPROSIUM **Dy** 162.50	67 HOLMIUM **Ho** 164.93	68 ERBIUM **Er** 167.26	69 THULIUM **Tm** 168.934	70 YTTERBIUM **Yb** 173.04
	89 ACTINIUM **Ac** 227.03	90 THORIUM **Th** 232.038	91 PROTACTINIUM **Pa** 231.036	92 URANIUM **U** 238.029	93 NEPTUNIUM **Np** 237.048	94 PLUTONIUM **Pu** (244)	95 AMERICIUM **Am** (243)	96 CURIUM **Cm** (247)	97 BERKELIUM **Bk** (247)	98 CALIFORNIUM **Cf** (251)	99 EINSTEINIUM **Es** (252)	100 FERMIUM **Fm** (257)	101 MENDELEVIUM **Md** (258)	102 NOBELIUM **No** (259)

*Each element in the table is listed with (from top to bottom) its atomic number, its name, its symbol, and its atomic mass. Atomic mass numbers in parentheses are the mass numbers of the longest-lived isotope. Other atomic mass numbers are the average mass number of the naturally occurring isotopes.

†The names and labels for elements beyond number 103 are controversial. IUPAC initially ruled in favor of Latin names based on atomic number, but in 1994 a set of specific names and symbols was suggested. After considerable debate, a revised final list of names for elements 104-109 was issued on August 30, 1997. Temporary names were also assigned for elements 110 and 111. Various groups have suggested alternatives names for some of these elements. Additional elements continue to be synthesized, though with increasing difficulty, with no definite upper atomic-number limit yet established.

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d

D, Vitamin ***See Cholecalciferol.***

Dalton, John

ENGLISH CHEMIST
1766–1844

The fundamental idea of modern chemistry is that matter is made up of atoms of various sorts, which can be combined and rearranged to produce different, and often novel, materials. The person responsible for "this master-concept of our age" (Greenaway, p. 227) was John Dalton. He applied Newton's idea of small, indivisible atoms to the study of gases in the atmosphere and used it to advance a quantitative explanation of chemical composition. If French chemist Antoine Lavoisier started the chemical revolution, then it was Dalton who put it on a firm foundation. His contemporary, the Swedish chemist Jöns J. Berzelius, said: "If one takes away from Dalton everything but the atomic idea, that will make his name immortal."

John Dalton was born on or about September 6, 1766, to Quaker parents, in Eaglesfield, a remote village in the north of England. He was largely self-educated, and learned most of his mathematics and science by teaching others. He studied mathematics in a local school until the age of 11, started his own school at the age of 12, and at 15 joined his brother Jonathan in teaching at, and later running, a Quaker school in Kendal. The Quakers were a small dissenting (from the established Church of England) sect, and Dalton was thus a nonconformist, like the scientists Joseph Priestley and Michael Faraday. Dalton was taught and influenced by fellow Quakers Elihu Robinson, a wealthy instrument maker, and John Gough, a blind polymath. In Kendal Gough taught the young Dalton Latin, Greek, French, mathematics, and science, and in return Dalton read to him from books and newspapers. Gough encouraged Dalton to study natural phenomena and to keep a meteorological journal, which Dalton began on March 24, 1787. Dalton maintained this journal methodically for the rest of his life, making his last meteorological observations on his deathbed. He made over 200,000 measurements over a period of fifty-seven years, and a neighbor in Manchester is supposed to have said that she was able to set her clock by Dalton's daily appearance to take the temperature. Dalton's meteorological observations launched his scientific career and provided the material for his first book, *Meteorological Observations and Essays* (1793).

British chemist and physicist John Dalton, who drew up the first list of atomic weights.

In 1793 Dalton moved to Manchester, becoming professor of mathematics and **natural philosophy** at New College. He stayed there until 1799, at which time he resigned in order to devote more time to research. He continued to teach private pupils in order to earn a living. According to legend, a visiting French scientist once traveled to Manchester to meet the famous Dalton. He had difficulty in finding him, finally locating him in a small house in an obscure street. He then had to wait while Dalton finished teaching a lesson in mathematics to a small boy.

Dalton stayed in Manchester for the rest of his life, and it was there that he did most of his important work, the results of which were published in the *Memoirs* of the Manchester Literary and Philosophical Society (MLPS). His first scientific paper, published by the MLPS in 1798, described his red-green color blindness. Dalton is said to have purchased for his mother a pair of what he thought were dull-colored stockings—Quakers did not wear bright colors—which she could not wear because they were scarlet. This misadventure motivated Dalton to investigate his color recognition deficiency. He was the first to describe red-green color blindness, sometimes known as Daltonism.

natural philosophy: study of nature and the physical universe

partial pressure: portion of a total pressure of a gas mixture contributed by a single type of gas in the sample

Dalton's study of the atmosphere, prompted by his weather measurements, led him in 1803 to his law of **partial pressures** (in a mixture of gases, each gas acts as an independent entity), and subsequently to the study of the combining of elements. He compared marsh gas (methane, CH_4) with olefiant gas (ethane, C_2H_4), and found that ethane contained exactly double the mass of carbon to the same mass of hydrogen. It is this relationship between the two gases that guided him to his law of multiple proportions. He imagined a chemical atomic model, whereby one atom of an element could combine only with one, two, or three atoms (and so on) of a second element, the combinations forming distinct compounds. He visualized atoms as small hard balls and constructed small wooden models to illustrate how they combined. He invented symbols that enabled him (and others) to notate chemical formulas ✷. Dalton drew up the first list of atomic weights. Dalton's ideas about atoms and their combinations were first aired in 1803 at meetings of the MLPS, mentioned in Thomas Thomson's *System of Chemistry* (1807), and finally published by Dalton in his most important book, *New System of Chemical Philosophy* (1808).

✷See an image of Dalton's symbols in the Atoms article.

Dalton's most significant work was done between 1795 and 1805, but fame came later—when the importance of his **atomic theory** was realized. He became a member of the **Royal Society** in 1822, received its first Royal Medal in 1826, and was honored with a state pension in 1833, among other honors. He died on July 27, 1844, and 40,000 people attended his funeral. SEE ALSO Berzelius, Jöns Jakob; Faraday, Michael; Lavoisier, Antoine; Priestley, Joseph.

Peter E. Childs

atomic theory: concept that asserts that matter is composed of tiny particles called atoms, the particular characteristics of which determine the type and form of the matter

Royal Society: The U.K. National Academy of Science, founded in 1660

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Databases *See Chemical Informatics.*

Davy, Humphry

ENGLISH CHEMIST
1778–1829

English chemist Sir Humphry Davy, who developed the first coherent theory of electrochemical action.

Sir Humphry Davy, the son of woodcarver, was born on December 17, 1778, in Penzance, Cornwall, then a highly industrialized area in the far west of England. In 1798 he moved to Bristol to work at the Pneumatic Institution under Thomas Beddoes, a physician who used gases for medicinal purposes. There he discovered the physiological properties of nitrous oxide (laughing) gas, which established his reputation as a chemist. In Bristol he became friends with the poets Samuel Taylor Coleridge and Robert Southey. No mean poet himself, Davy, at the suggestion of his friends, saw the second edition of William Wordsworth's *Lyrical Ballads*—that seminal text of English Romanticism—through to publication.

In 1801, at the age of twenty-two, Davy was appointed assistant professor and director of the laboratory at the newly founded Royal Institution (1799), and the following year he became professor of chemistry. In the eleven years that he was there, Davy firmly established the Royal Institution's reputation for excellent lectures on science and other areas of culture (he even influenced Coleridge to lecture there). In addition, he was a strong supporter of the utilitarian function of the Royal Institution, particularly in its application of chemical knowledge to the improvement of agriculture and industrial processes, in both of which Davy played a major role. But Davy also transformed the Royal Institution into a setting where in-depth scientific research would be carried out, something that its founders had not planned. But because of its commitment to providing spectacular lectures, the Royal Institution quickly came to have one of the best equipped laboratories in Europe, where research could be conducted.

During the first decade of the nineteenth century, Davy undertook fundamental work on electrochemistry following Alessandro Volta's invention of the electric battery at the end of the eighteenth century. Davy developed the first coherent theory of electrochemical action, whereby he argued that electrochemical decomposition took place at the **metal** poles through which electricity passed into a compound. Indeed, Davy posited that electrical force was the basis of all chemistry. During the course of his work, he discovered sodium and potassium, and later magnesium, calcium, strontium, and barium. Using the same electrochemical techniques, Davy eventually showed that chlorine and iodine were chemical elements rather than compounds, contrary to what French chemists had believed.

metal: element or other substance the solid phase of which is characterized by high thermal and electrical conductivities

In 1812 he was knighted by the prince regent for his contributions to electrochemistry, married a wealthy widow Jane Apreece, and was thus able to retire from the Royal Institution at the age of thirty-four, although he remained the director of its laboratory. It was in this capacity that he appointed Michael Faraday as an assistant in the laboratory early in 1813. Later that year with his wife, her maid, and Faraday as an assistant, amanuensis (scribe), and reluctant valet, Davy embarked on an eighteen-month tour of the European continent, visiting many laboratories and sites of natural and cultural interest. On their return, Davy invented, with Faraday's assistance, the miners' safety lamp, which reinforced his reputation in applied science. With a confidence that was shared by all romantics of the time, Davy believed that nothing was beyond his reach, and in 1820 he was elected president of the **Royal Society**. This was a position he was ill-equipped to undertake after the forty-two-year presidency of Joseph Banks. Banks had been an autocratic president, and Davy had neither the ability to continue to lead in that mode, nor the power to take the society in a different direction. Davy sought to keep the peace between various factions within the society, but without success. His hostile attitude toward Faraday at this time was largely governed by the politics of the Royal Society. Davy's frustrations were compounded in the mid-1820s when his attempts to develop an electrochemical method for protecting the copper sheeting of the Royal Navy's ships failed. This resulted in strained relations between the government and the Royal Society, which culminated in the government abolishing the Board of Longitude, the only body then channeling state money into science. Davy suffered a stroke and resigned the presidency in 1827; he subsequently traveled abroad, where he died in Geneva, Switzerland, on May 29, 1829. Despite the ups and down of his career, during the nineteenth century Davy came to be regarded as a towering figure and a comparison with him was an enormous compliment. SEE ALSO BARIUM; CALCIUM; FARADAY, MICHAEL; MAGNESIUM; POTASSIUM; SODIUM; STRONTIUM; VOLTA, ALESSANDRO.

Royal Society: The U.K. National Academy of Science, founded in 1660

Frank A. J. L. James

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de Broglie, Louis

FRENCH PHYSICIST
1892–1987

Louis-Victor-Pierre-Raymond de Broglie was born into a noble French family. He initially studied history at the Sorbonne in Paris, intending to enter the diplomatic service. His elder brother Maurice had chosen to forgo a diplomatic career for one in physics, despite opposition from his family. Louis also became interested in science and decided to pursue a degree in **theoretical physics**. His plans, however, were interrupted by World War I, during which time he served in a wireless telegraphy unit stationed at the Eiffel Tower.

theoretical physics: branch of physics dealing with the theories and concepts of matter, especially at the atomic and subatomic levels

In 1920 de Broglie returned to his studies; later he stated that his attraction "to theoretical physics was . . . the mystery in which the structure of matter and of radiation was becoming more and more enveloped as the strange concept of the quantum, introduced by Max Planck in 1900 in his researches into black-body radiation, daily penetrated further into the whole of physics" (quoted by Heathcote, pp. 289–290).

During this same period de Broglie's brother Maurice was studying experimental physics, and he was particularly interested in x rays. The brothers frequently discussed x rays, and their dual nature (both wavelike and particle-like behavior) suggested to Louis that this same particle-wave duality might also apply to particles such as electrons.

In his doctoral dissertation in 1924, Louis de Broglie developed the equation $\lambda = h/mv$, which predicts that the wavelength λ of a particle is inversely proportional to its mass m and velocity v, where h is Planck's constant.✷ The wavelength associated with a submicroscopic object—an electron, for example—is large relative to the size of the object and is therefore significant in describing its behavior, whereas the wavelength associated with a macroscopic object—a basketball, for example—is negligibly small relative to its size, and therefore the wavelike behavior of such an object is unnoticeable.

✷See Max Planck article for more about Planck's constant.

The dual nature of electrons proposed by de Broglie, together with the dual nature of electromagnetic radiation proposed by Max Planck, led to the development of **quantum mechanics** by the Austrian physicist Erwin Schrödinger in 1926. The following year American physicists Charles J. Davisson and Lester H. Germer and others demonstrated experimentally that electrons can be diffracted just like light. That is, as electrons pass through a narrow slit, they spread out in a wavelike pattern similar to that of diffracted light.

quantum mechanics: theoretical model to describe atoms and molecules by wave functions

De Broglie accomplished his most important work in physics while still a young man, receiving the Nobel Prize in physics in 1929. After obtaining his doctorate in 1924, he taught at the Sorbonne, and in 1928 he was named professor of theoretical physics at the Henri Poincaré Institute in Paris. In 1932 he also became professor of theoretical physics at the Sorbonne, retiring from that post in 1962.

Throughout his long life, de Broglie remained active in the development and interpretation of quantum mechanics and wrote more than twenty-five books on various topics related to this field of study. As a member of the French Commission on Atomic Energy, he was a long-time advocate for the peaceful use of atomic power. De Broglie also wrote a number of popular books to help promote public understanding of modern physics, and in recognition of these efforts, the United Nations Educational, Scientific, and Cultural Organization (UNESCO) awarded him the Kalinga Prize in 1952. He was the recipient of many awards and honors for his work in quantum mechanics.

As a young scientist de Broglie had believed that the statistical nature of modern physics masks our ignorance of the underlying reality of the physical world, but for much of his life he also believed that this statistical nature is all that we can know. Toward the end of his life, however, de Broglie turned back toward the views of his youth, favoring causal relationships in place of the accepted probabilistic picture associated with quantum mechanics. SEE ALSO PLANCK, MAX; SCHRÖDINGER, ERWIN

Richard E. Rice

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Denaturation

Protein molecules carry out many important tasks in living systems. Most important, the majority of proteins are quite specific about which task they perform. Protein structure is what dictates this specificity, and the three-dimensional (tertiary) structure is particularly important. When this specific three-dimensional structure is disrupted, the protein loses its functionality and is said to have undergone denaturation.

hydrogen bonding: intermolecular force between the H of an N–H, O–H, or F–H bond and a lone pair on O, N, or F of an adjacent molecule

The interactions, such as **hydrogen bonding**, that dictate the tertiary structure of proteins are not as strong as covalent chemical bonds. Because these interactions are rather weak, they can be disrupted with relatively modest stresses.

If a solution containing a protein is heated, it will reach a temperature at which properties such as viscosity or the absorption of ultraviolet (UV) light will change abruptly. This temperature is called the melting temperature of the protein (because the measurement is analogous to that made for the melting of a solid). The melting temperature varies for different proteins, but temperatures above 41°C (105.8°F) will break the interactions in many proteins and denature them. This temperature is not that much higher than normal body temperature (37°C or 98.6°F), so this fact demonstrates how dangerous a high fever can be.

An egg white before the denaturation of the albumin protein causes the transucent substance to change in color and viscosity.

A familiar example of heat-caused denaturation are the changes observed in the albumin protein of egg whites when they are cooked. When an egg is first cracked open, the "whites" are translucent and runny (they flow like a liquid), but upon heating they harden and turn white. The change in viscosity and color is an indication that the proteins have been denatured.

Factors other than heat can also denature proteins. Changes in pH affect the chemistry of amino acid residues and can lead to denaturation. Hydrogen bonding often involves these side changes. Protonation of the amino acid residues (when an acidic proton H^+ attaches to a lone pair of electrons on a nitrogen) changes whether or not they participate in hydrogen bonding, so a change in the pH can denature a protein.

Changes in salt concentration may also denature proteins, but these effects depend on several factors including the identity of the salt. Some salts, such as ammonium sulfate, tend to stabilize protein structures and increase the melting temperature. Others, such as calcium chloride, destabilize proteins and lower the melting temperature and are called chaotropic. Salts in this category can also be used in the laboratory to help purify proteins that are being studied, by lowering their solubility and causing them to "salt out." SEE ALSO Heavy Metal Toxins; Proteins.

Thomas A. Holme

The heat-caused denaturation in albumin protein in egg whites causes the once translucent, runny substance into one that is white and firm.

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Deoxyribonucleic Acid (DNA)

Deoxyribonucleic acid (DNA) is the genetic material of most living organisms. One of its main functions is to produce ribonucleic acid (RNA), which then makes proteins. Thus, information within DNA allows a cell to make most of the molecules it needs to function.

DNA and RNA are nucleic acids that are composed of sugars, phosphates, and nitrogenous bases (or a base). The four bases found in DNA are **guanine** (G), **cytosine** (C), thymidine (T), and **adenine** (A). Each sugar attached to a base and phosphate is called a nucleotide. Hence, DNA is a collection of nucleotides.

Bases from two different strands interact to form a double-helical structure. Guanine forms three **hydrogen bonds** with cytosine, whereas adenine forms two hydrogen bonds with thymidine. **Stacking interactions** between the planar bases also stabilize the DNA structure. Phosphates and sugars form the backbone of DNA.

The DNA sequence is represented by writing the base sequence from the **5′ end** to the **3′ end** of one strand, for example, 5′-GATTACA-3′ represents:

5′-GATTACA-3′
3′-CTAATGT-5′

The sugars and phosphates are omitted in this notation. A comparison of DNA sequences comparison allows one to determine the relationship between different organisms and is also used to find small differences in humans (so-called DNA fingerprinting). SEE ALSO Nucleic Acids; Nucleotide; Ribonucleic Acid.

Neena Grover

guanine: heterocyclic, purine, amine base found in DNA

cytosine: heterocyclic, pyrimidine, amine base found in DNA

adenine: one of the purine bases found in nucleic acids, $C_5H_5N_5$

hydrogen bond: interaction between H atoms on one molecule and lone pair electrons on another molecule that constitutes hydrogen bonding

stacking interactions: one type of interaction that affects conformation of double-stranded DNA; caused by van der Waals forces

5′ end: situation in nucleic acids in which the phosphate group is attached at the fifth carbon atom from where the base is attached

3′ end: situation in nucleic acids in which the phosphate group is attached at the third carbon atom from where the base is attached

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Detergents

Soap and cleanliness are inseparable, and cleansing, be it personal hygiene or laundering, is part of human history. Stringent guidelines with regard to the cleanliness of holy sites are a part of all the major religions, and the sanctification of the state of cleanliness as well as its signification of purity of body and soul are recurrent themes in their liturgies.

The origins of the word "soap" and of the first use of soap are obscure. According to one Roman legend, soap was discovered serendipitously near Mount Sapo, an ancient location for animal sacrifice not far from Rome. Animal fat mixed with wood ashes (the ancient source of alkali) and rainwater created an excellent soap mixture. Roman housewives noticed that the strange yellow substance in the water of the Tiber River (flowing near Mount Sapo) made their clothes cleaner and brighter than ordinary water.

Soapmaking became an art among the Phoenicians (fl. ca. 600 B.C.E.) and underwent significant advances in Mediterranean countries in which local olive oil was boiled with alkali ashes (as part of soapmaking) at around the same time.

Ascribing value to cleanliness seems to have been a part of the civilizing of humankind. After the fall of Rome (in 467 C.E.), a decline in attention paid to personal cleanliness and the maintenance of sanitation contributed to the great plague of the Middle Ages, and made especially grim contributions to the Black Death plague epidemic of the fourteenth century. Cleanliness and regular bathing became unremarkable in much of Europe not until 300 years later.

ester: organic species containing a carbon atom attached to three moieties: an O via a double bond, an O attached to another carbon atom or chain, and an H atom or C chain; the R(C=O)OR functional group

For several centuries in Europe, soapmaking was limited to small-scale production that often used plant ashes containing carbonate (**esters** of carbonic acid) dispersed in water, which were then mixed with animal fat and boiled until the water evaporated. The reaction of fatty acid with the alkali carbonate of the plant ashes formed a soap and glycerol.

The real breakthrough in soap production was made in 1780 by a French chemist and physician, Nicolas Leblanc, who invented the process of obtaining soda (sodium carbonate, Na_2CO_3) from common salt (the Leblanc process), and increased the availability of this alkali at a reasonable cost. With the development of power to operate factories, soapmaking grew from a "cottage industry" into a commercial venture and became one of the fastest-growing industries of the modern era. Body soap, which had been a luxury item affordable by royalty and the very rich, became a household item of ordinary folks as well.

etiology: causes and origins of a disease

Throughout the nineteenth century, physicians were realizing the value of soap as a medicinal agent. A well-known protagonist of soap was scientist and educator Ignaz Phillipp Semmelweis, who in 1847 discovered the infectious **etiology** of puerperal fever and therefore required medical students to wash their hands before they examined patients. Semmelweis encouraged

INGREDIENTS OF SOAP, SHAMPOO, AND DETERGENT

Ingredients	Percent of Total by Weight
Surfactants	30-70
Plasticizers and binders	20-50
Lather enhancers	0-5
Fillers and binders	5-30
Water	5-12
Fragrance	0-3.0
Opacifying agents	0-0.3
Dyes and pigments	<1

Table 1. Ingredients of soaps and detergents.

his colleagues to adopt his antiseptic methods, telling them, "while we talk, talk, talk, gentlemen, women are dying. I am not asking anything world-shaking. I am asking you only to wash. . . . For God's sake, wash your hands." In a circular handed out in Budapest during the summer of 1865, he implored new mothers: "Unless everything that touches you is washed with soap and water and then chlorine solution, you will die and your child with you!"

The chemistry of soap manufacturing stayed essentially unchanged until World War II, at which time synthetic detergents (syndets) became available. There had been a search for cleansing agents that would foam and clean when added to seawater in response to the need of sailors who spent months at sea under severe freshwater restrictions.

The Chemistry of Soaps, Shampoos, and Laundry Detergents

Soaps, shampoos, and laundry detergents are mixtures of ingredients (see Table 1). The **surfactants** are the essential cleaning substances and they determine the cleansing and lathering characteristics of the soap, as well as its texture, plasticity, abrasiveness, and other features. Surfactants are compounds that have a dual affinity: They are both **lipophilic** and **hydrophilic**. A surfactant molecule consists of a lipophilic tail group, which links to greasy soil, and a hydrophilic and polar head group, which renders the molecule water-soluble; this arrangement helps to disperse and rinse away greasy soil. Variations in the balance between **hydrophobic** and hydrophilic features determine the use of the surfactant as a detergent, **wetting agent**, or **emulsifier**.

surfactants: surface-active agents that lower the surface tension of water; e.g., detergents, wetting agents

lipophilic: a molecule that tends to associate in solution with lipids—it will be a nonpolar molecule or the nonpolar portion of a molecule

hydrophilic: having an affinity for water

hydrophobic: repelling water

wetting agent: molecule that, when added to a liquid, facillitates the spread of that liquid across a surface

emulsifier: substance that stabilizes the formation of an emulsion—normally it contains molecules with both polar and nonpolar functional groups

Surfactants are classified according to the nature of the hydrophilic head. There are four main classes: anionic, cationic, amphoteric, and nonionic. The first three refer to charged surfactant molecules. An anionic surfactant possesses a negative charge and needs to be neutralized with an alkaline or basic material in order for its full detergent capacity to be realized, whereas a cationic surfactant is positively charged and needs to be neutralized by an acid. Amphoterics include both acidic (negative) and basic (positive) groups, and nonionics contain no ionic constituents. "Natural" soap contains an anionic surfactant. The majority of surfactants that are used in personal cleansing bars and shampoos have anionic head groups.

It is noteworthy that almost all anionic surfactants are sodium or potassium salts of the negatively charged head groups; thus the advertising slogans "alkali free" and "soapless soap" are incorrect. Most soaps and shampoos contain a mixture of two to four surfactants (out of the thousands of synthetic surfactants that are currently available). In addition, there are innumerable plasticizers, binders, moisturizers, and fillers that are also used to formulate these soaps and shampoos. Creation of the formula of a soap is a complicated enterprise and it requires, in addition to a knowledge of chemistry and even engineering, both imagination and inspiration. The contemporary formulation of soaps is the result of research and development, as well as trial and error, carried out over a course of many years by research teams. It is as much art as it is science, and it requires a long learning experience.

The Process of Washing

The most obvious target of cleansing is the outermost layer of the skin, the keratinizing epithelium. It is a cornified (hardened) cell envelope and it has an extremely tough protein/**lipid** polymer structure. This hard and lipophilic layer of the epidermis and the surface hairs would not easily retain dirt if it were not for a hydrolipid film that covers the outermost layer of skin and that picks up particles of soil. This natural outer film of lipid entraps and glues environmental dust, pollutants, smoke, keratinous debris, organic and inorganic compounds in sweat, cosmetics, and other substances that come in contact with it. The hair of the scalp (corresponding to a surface area of about 8 square meters, or 86 square feet, for an average female head) is cleansed regularly. The scalp gets coated with sebum, the product of the sebaceous appendages that flows into hair follicles and a natural lubricating oil that contributes luster to the hair, on the one hand, but entraps dirt, on the other.

lipid: a nonpolar organic molecule; fatlike; one of a large variety of nonpolar hydrophobic (water-hating) molecules that are insoluble in water

Washing the skin consists of the removal of the outer layer of grease (lipid) in which the soil (no matter what kind) is embedded. It is a complex physicochemical process that includes the following:

1. A weakening of the binding forces between the keratinized epithelium and the layer of grease via the reduction of the surface tension between the water and the water-resistant oil/grease. Because of this reduced surface tension, water (and surfactant molecules) can penetrate into the finest wrinkles of the skin. In this way, more and more interface is occupied by surfactant, and the adhesiveness of the soil-containing layer is further weakened, a process facilitated by mechanical rubbing.
2. Transfer of portions of the layer of oil to the aqueous vehicle. It is facilitated by the action of the micelles created when the soil was emulsified. The micelles have negatively charged surfaces and are repulsed by the overall negative charge of the keratin of the skin epithelium.
3. Dispersion/suspension of the oil and dirt particles in the soap foam, preventing these particles from being redeposited on the surface.

The Interaction of Soaps with the Skin

Surgeons need to scrub. Health-care providers and employees of food services must take a range of precautions against the dissemination of microorganisms. Very often, the simple act of washing one's hands is not fateful but nevertheless wise. Most experts in infection control and epidemiology maintain that hand washing remains the most powerful defense against infections. Germs are all around us, and can linger anywhere: the office phone, door handles, shopping baskets, money, even the button you push when you call for an elevator. You can unknowingly come into contact with germs. One simple rub of the eye or bite of a sandwich using unwashed hands can introduce any number of illnesses into your body. Hand washing reduces the risk. At the same time, most contemporary dermatologists agree that the comfortable classes have become preoccupied with cleanliness. Less, not more, washing is better for the skin. However, the irritant, toxic, and harmful effects of soaps have been exaggerated by some advertisers. (After all, what better way to promote their "mild," "nonallergenic," and "soapless" products?)

Washing with soap makes no discretely identifiable contribution to health. Its value lies more in the feeling it engenders in the user. People derive great enjoyment from washing: It gives them a tremendous sense of well-being. SEE ALSO BLEACHES; HAIR DYES AND HAIR TREATMENTS; LEBLANC, NICOLAS.

Ronni Wolf

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Dewar, James

BRITISH CHEMIST AND PHYSICIST
1842–1923

Sir James Dewar was born in Kincardine, Scotland, on September 20, 1842, the son of an innkeeper. He attended local schools until he was ten when he suffered a serious case of rheumatic fever lasting two years. During this period he built a violin, and music remained a lifelong interest of his. In 1858 he entered the University of Edinburgh. There he studied physics and chemistry. Dewar, in an early display of his dexterity, developed a mechanical model of Alexander Crum Brown's graphic notation for organic compounds. This was sent to Friedrich Kekulé in Ghent who then invited Dewar to spend some time in his laboratory.

After holding a number of chemical posts in Scotland, Dewar was appointed Jacksonian Professor of **Natural Philosophy** at the University of Cambridge in 1873, and four years later he was appointed Fullerian Professor of Chemistry at the Royal Institution. He held both chairs concurrently, but spent most of his time in London. At Cambridge he collaborated with George Downing Liveing on an extensive **spectroscopic** study linking spectra with atomic and molecular states. This led to a very public disagreement with Norman Lockyer about the dissociation of matter in the Sun and stars. One of Dewar's chief characteristics was his ability to engage, at times, in quite vitriolic arguments with other scientists; Robert John Strutt, the fourth Lord Rayleigh wrote that to argue with Dewar was akin to being a fly in molasses.

natural philosophy: study of nature and the physical universe

spectroscopy: use of electromagnetic radiation to analyze the chemical composition of materials

Scottish chemist and physicist Sir James Dewar, the first person to liquefy hydrogen.

Joule–Thomson effect: the change in temperature of a gas when it is compressed or allowed to expand through a small opening

At the Royal Institution, Dewar found himself at the intersection of major scientific networks involving the government and industry. He thus collaborated in the late 1880s with Frederick Abel on the invention of the explosive cordite. Nevertheless, at the Royal Institution Dewar focused almost entirely on cryogenics. In 1877 oxygen had been liquefied in France, and the following year Dewar demonstrated this for the first time in England at a lecture at the Royal Institution. New methods for obtaining low temperatures were developed in the 1880s, but Dewar's ability to take advantage of these methods was restricted by his not being fully in charge of the Royal Institution. However, after forcing John Tyndall's retirement in 1887, Dewar became the director of its laboratory. He improved low-temperature methods, especially by the application of the **Joule–Thomson effect** that produced much lower temperatures. Dewar had now turned his attention to hydrogen, which he could not liquefy even at the low temperatures obtainable.

In the mid-1890s Dewar was responsible for one of the most important developments in the history of the Royal Institution: the establishment and endowment of the Davy–Faraday Research Laboratory of the Royal Institution. This not only entailed the acquisition of a new building, but also the direct support of Dewar's cryogenic research. Success came in 1898 when he finally liquefied hydrogen. However, in the race with Heike Kamerlingh Onnes at the University of Leiden to liquefy helium, Dewar lost and the Nobel Prize went to Kamerlingh Onnes. Although Dewar was nominated several times, he never won the coveted prize.

One of the consequences of Dewar's work was his invention of the vacuum flask to minimize heat loss. It was expensive and time-consuming to liquefy gases; hence, Dewar designed a container where, once liquefied, gases could be kept for as long as possible. Still known as the Dewar flask among chemists, it is more widely known as the Thermos, named after the company that obtained the patent for the flask and to whom Dewar lost an ensuing court case.

Dewar's later work involved investigating the chemical and physical properties of substances at low temperatures, including low-temperature calorimetry. With the outbreak of the Great War (or World War I, 1914–1918), the laboratory at the Royal Institution lost most of its staff and Dewar turned his attention to soap bubbles. By the end of the war Dewar, now in his late seventies, did not have the energy to restart the laboratory, nor would he retire. He died on March 27, 1923, and his funeral service was held in the director's flat at the Royal Institution. SEE ALSO KEKULÉ, FRIEDRICH AUGUST.

Frank A. J. L. James

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Digital X Ray

X-ray technology provides physicians and technicians with a noninvasive method for seeing inside objects. In the case of a patient's body, this may allow diagnosis of disease or injury without surgery. Both conventional and digital x-ray methods employ high **voltage** electronic tubes such as synchrotons that emit very short wavelength, high energy electromagnetic radiation in the range of 10^{-11}–10^{-8} meters (3.28×10^{-10}–3.94×10^{-6} feet) (a frequency of about 3×10^{19} Hz to 3×10^{16} Hz). One Hz (Hertz) is equal to 1 cps (cycle per second).

voltage: potential difference expressed in volts

Unlike longer-wavelength, lower-frequency visible light, x-ray radiation consists of waves so small that they can pass through solid materials with little effect. As the radiation moves through materials of different densities (bone and tissue, for example), some waves are blocked and produce shadows that result in light-and-dark images. Some materials, such as bone or metal, are opaque and appear as light areas, while other materials such as air in body cavities allow most of the x-ray waves to pass through, producing dark areas in the image.

Conventional x-ray images are captured by special photographic film, sensitized with silver salts that are converted by developing processes to dark and light images. Photons striking a photographic **emulsion** convert some silver ions to tiny particles of silver that grow large enough during the process of developing to form tiny grains in the photographic negative. Digital x-ray processes use individual crystal **photodiode assemblies** (each photodiode acts as a very small light-sensitive transistor, using the light energy from individual photons to modulate an electrical current flowing through the diode) containing compounds such as cadmium tungstate or bismuth germanate to capture light energy as electrical pulses that are then converted from analog to digital signals, stored in computer memory, and processed to form visual images on computer screens. Because electronic sensors may be more sensitive than film, digital x-ray processes may use as little as 10 percent of the energy needed for conventional x rays (and may thus require less massive shielding).

emulsion: immiscible two-phase mixture in which one phase is dispersed (as small droplets) in the other phase

photodiode assembly: grouping of electronic devices that includes a photodiode—a photodetector; useful in medical diagnostics, bar code readers, and guidance systems

Although different types of x-ray technology may be ideally suited to different applications, the use of electronic sensors and digital technology offer several advantages over conventional x rays. The capture of an image by a photosensitive electronic device is rapid and allows the image to be enlarged, colored, or adjusted in density. In addition, the use of electronically captured images may be less expensive, allowing computer-assisted data processing and storage. Conventional x-ray film must be developed, washed, fixed, and dried, requiring chemical substances that may be harmful to the environment, and the resulting images on film may require massive storage facilities.

Digital x rays can be modified electronically to increase contrast, display certain structures in color or three dimensions, or subtract areas that interfere, allowing clearer pictures of structures such as veins and arteries. Very small differences in density may be amplified for even clearer viewing. This may be important in cases in which a contrast medium is injected into veins or arteries; enhancing small differences allows the use of smaller amounts of the contrast medium, lessening the danger to patients.

This patient is undergoing cerebral angiography. Digital x rays use electronic signals to form visual images, rather than the photographic method of the conventional x ray.

After digital x-ray images have been obtained, they may be easily copied, displayed, stored electronically, shared with patients, or sent to remote locations for examination by highly trained technicians. The images may be conveniently linked to other equipment or processes such as CAT (computer axial tomography) scans or three-dimensional displays. Digital technology may also be employed in security applications for the remote scanning of packages and luggage. SEE ALSO Selenium.

Dan M. Sullivan

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Disaccharides

Sucrose, or table sugar, is the most common disaccharide. Although the term "sugar" is commonly used to refer to sucrose, sucrose is only one of a large group of sugars. Disaccharides are carbohydrates containing two **monosaccharides** linked by a glycosidic bond. Glycosidic bonds form when the anomeric carbon of one sugar reacts with a hydroxyl group belonging to a second sugar. Sugars with free anomeric carbons can reduce **ferric** (Fe^{3+}) and cupric (Cu^{2+}) ions, and are called reducing sugars. Anomeric carbons

monosaccharide: one class of the natural products called carbohydrates with the general formula $C_x(H_2O)_y$; monosaccharides have a weak sweet taste, are readily soluble in water, and are called sugars

ferric: older name for iron in the +3 oxidation state involved in glycosidic bonds are nonreducing. In general, disaccharides and polysaccharides contain both reducing and nonreducing sugars. These carbohydrates are represented and their formulas are written from nonreducing end to reducing end.

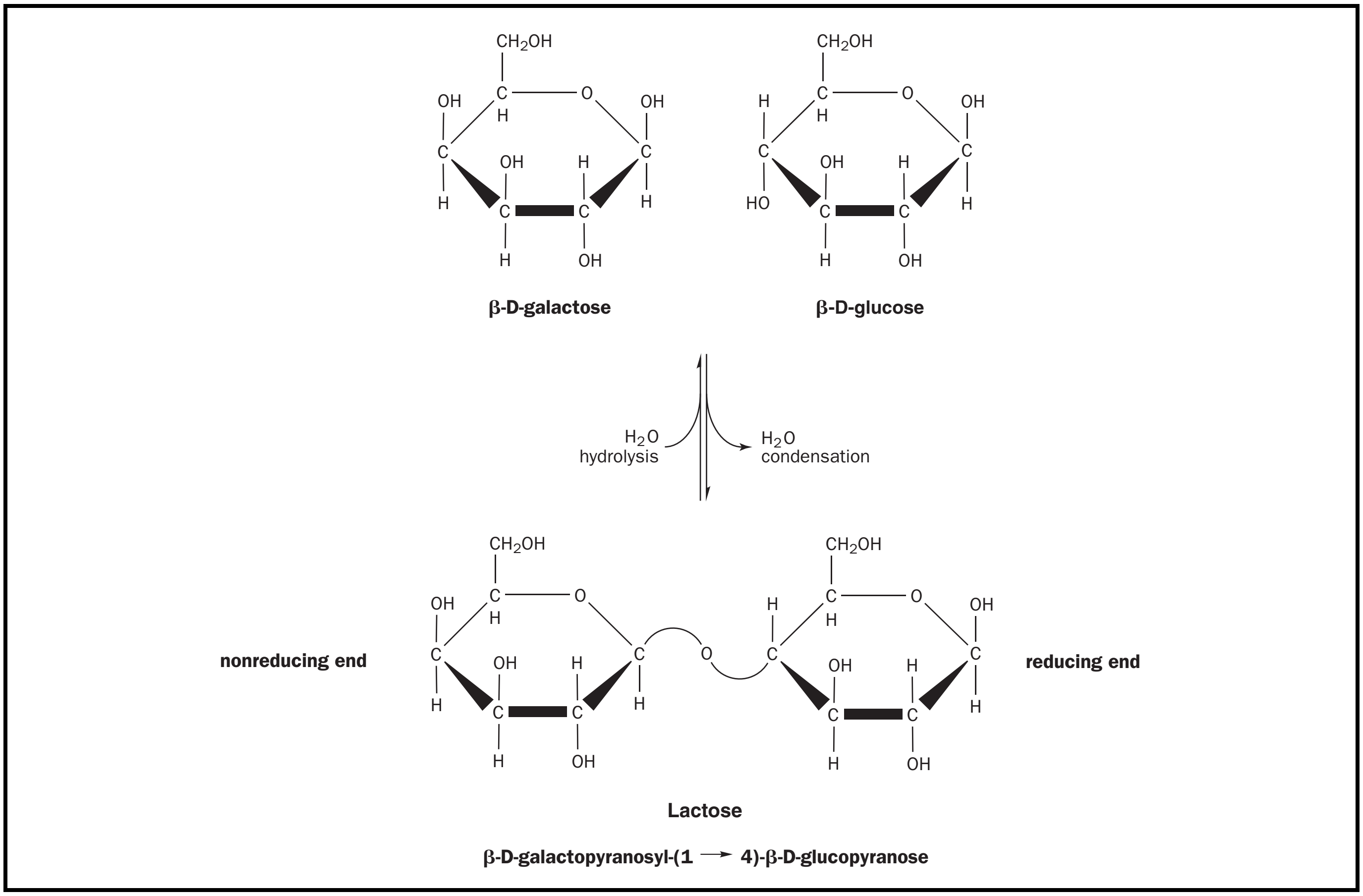
A common disaccharide is lactose, which is found only in milk. Lactose is formed from monosaccharides *β*-D-**galactose** and *β*-D-**glucose**. The anomeric carbon of the *β*-D-galactose molecule reacts with the C-4 hydroxyl group of the *β*-D-glucose molecule to form the glycosidic bond (see Figure 1). The bond is designated a *β*(1→4) bond, indicating the configuration of the anomeric carbon (*β*), the number of the anomeric carbon (1), and the number of the carbon (of the second sugar) to which it is linked (4). The correct specification of the configuration of the anomeric carbon is critical: an *α*(1→4) linkage is not the same thing as a *β*(1→4) linkage. Lactose is a reducing sugar; the *β*-D-glucose residue has a free anomeric carbon, and therefore the glucose residue is on the reducing end.

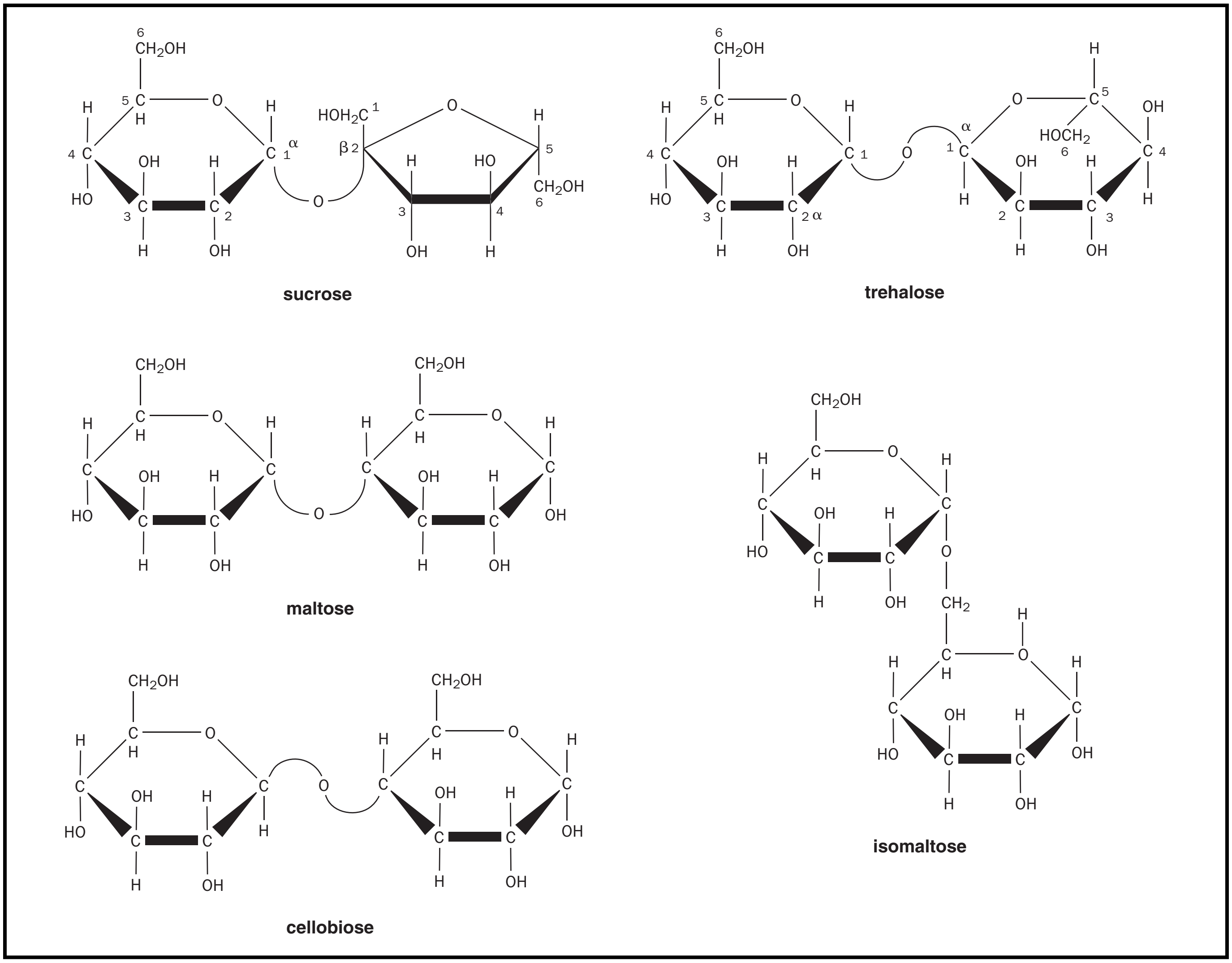
galactose: six-carbon sugar

glucose: common hexose monosaccharide; monomer of starch and cellulose; also called grape sugar, blood sugar, or dextrose

Lactose is hydrolyzed to glucose and galactose in the intestine by the enzyme lactase. People who are lactose-intolerant lack this enzyme. In these people, lactose advances in the digestive tract to the large intestine, where it is fermented by intestinal bacteria to produce large amounts of carbon dioxide and organic acids. Today, people with lactose intolerance can purchase milk in which the lactose has already been hydrolyzed, or can buy lactase supplements.

Figure 1. Formation of a glycosidic bond.




sucrose

trehalose

maltose

isomaltose

cellobiose

Figure 2. Selected disaccharides.

photosynthesis: process by which plants convert carbon dioxide and water to glucose

In contrast, most people are fond of and tolerate sucrose (see Figure 2). Sucrose is produced by plant cells; it is one of the major products of **photosynthesis**. It contains glucose and fructose molecules linked across the anomeric carbons of both (the C-1 of glucose and the C-2 of fructose). The systematic name is α-D-glucopyranosyl-(1→4)-β-D-fructofuranoside. Because it lacks a free anomeric carbon, sucrose is a nonreducing sugar. Sucrose is hydrolyzed in the intestine by the pancreatic enzyme sucrase.

A third prevalent disaccharide is trehalose (see Figure 2). Like sucrose, trehalose is a nonreducing sugar. It is composed of two glucoses in an $\alpha(1\rightarrow1)\alpha$ linkage. Trehalose is the principal sugar in the hemolymph of insects.

Other disaccharides are the product of the breakdown of larger polysaccharides. Maltose, cellobiose, and isomaltose are all composed of glucose residues (see Figure 2). Maltose and isomaltose both contain α-glucoses: in $\alpha(1\rightarrow4)$ linkages in the case of maltose, and in $\alpha(1\rightarrow6)$ linkages in the case of isomaltose. Maltose results from the hydrolysis of starch, and isomaltose from the hydrolysis of dextrans. Cellobiose is composed of β-glucose occurring in $\beta(1\rightarrow4)$ linkages. It is a breakdown product of cellulose. SEE ALSO CARBOHYDRATES.

Stephanie E. Dew

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Disposable Diapers

During the past forty years, disposable diapers have become an important part of the economy. Since the average baby uses at least ten diapers per day for an average of two years, the convenience of the product has made it a very popular as well as controversial item. A recent survey by Texas A&M University reported that 81 percent of the participants exclusively used disposable diapers, 15 percent used cloth and disposables, while just 4 percent used only cloth diapers.

The disposable diaper of today is composed of an inner layer of polyester that allows liquids to pass through to a layer of absorbent material, and an outer waterproof plastic layer of polyethylene film. The design was developed by many researchers through trial and error.

History

It is not clear who should be credited as the inventor of the first disposable diaper. The need for disposable diapers arose during World War II because of a shortage of cotton, which was used in traditional diapers. One of the first effective disposable diapers was created by Marion Donovan during the postwar baby boom. She is also credited with inventing the first plastic covering for traditional cloth diapers. Using this plastic covering (made from a shower curtain) and layers of tissue paper as an absorbent inner material, Donovan devised the new diaper in 1950. These first diapers were rectangular in shape, resulting in a bulky fit. In the 1960s, pulp was substituted for the paper, improving the absorbency of the diaper. The top sheets of the diaper were modified by using rayon. These diapers still were quite thick and included no tape for closure. By the 1970s the demand for disposable diapers had increased, and more improvements were added. New tapes were added for ease of fastening, and the shape was changed from rectangular to "hourglass."

During the early 1980s, modifications were made to respond to the demand for a better-fitting and biodegradable product. Starch was added to the outer sheet to enhance its biodegradability. Elastic was added to the

This baby is wearing a disposable diaper. Various technologies have improved the fit, absorbency, and biodegradability of the product.

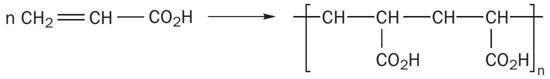
waist and to the leg openings for a better fit. Unfortunately this added a nonbiodegradable component to the product. A new tape system was developed to allow for several tapings and retapings without tearing the diaper. In response to a greater demand for a more environmentally friendly product, a new filler, cellulose mixed with crystals of polyacrylate, was developed. The cellulose is processed from pine trees and milled into "fluff pulp." The pulp consists of long cellulose fibers that provide a strong capillary effect, which helps to draw in the liquid. The surface tension binds the water once it has been absorbed.

The polyacrylate (known as a "superabsorbent polymer" or SAP by the diaper industry) is distributed throughout the fluff pulp. Another name for these crystals is Waterlock™. It is also used for plants to help retain water in the soil. The polyacrylate under pressure can hold an amount of liquid that is as much as thirty times its weight. This correlates to the compression (pressure) that occurs when a baby would sit or lie on the diaper. The polyacrylate allowed the manufacturers to reduce both the weight and thickness of the diaper by 50 percent and increase its absorbency.

Polymer Chemistry

The polyacrylate used in the diaper is a large-molecular-weight compound called a polymer. It consists of small repeating units called *monomers*. The length of the chain as well as the properties of the polymer may be changed by varying the reaction conditions. If two monomers are used in the **synthesis** of the polymer, the resultant polymer is referred to as a copolymer. The polymer used in disposable diapers is prepared by using acrylic acid as the monomer:

synthesis: combination of starting materials to form a desired product



$$n\,\mathrm{CH_2{=}CH{-}CO_2H} \longrightarrow \left[\mathrm{-CH-\underset{CO_2H}{CH}-CH-\underset{CO_2H}{CH}-} \right]_n$$

To obtain the properties needed for the diaper, sodium acrylate is used in the polymerization. The reaction is said to use "partially neutralized acrylic acid." The exact proportion of the two monomers (acrylic acid and sodium acrylate) present influences the character of the polymer formed. The length of the chains (represented by *n*) also is modified by reaction conditions and can change the characteristics of the polymer.

In addition to forming the chains of polyacrylate, the chains are cross-linked. This is a process in which two or more chains are held together by other compounds in a network. Typical cross-linkers for this polymer include di- and tri-acrylate esters. The swelling and elasticity of the polyacrylate polymer depends on the structure of this network and the number of cross-links. The swelling capacity of the polymer decreases with increased cross-link density. After formation, the polyacrylate is dried and formed into microparticles of irregular shape that can be stored for a long time.

When these particles come in contact with water, urine, or other **aqueous solutions**, they quickly swell and absorb the liquid. Typically it takes no more than five to ten seconds for this to occur. The ability to swell and absorb the water is dependent upon the **ionization** of the acid groups on the polymer chain. The amount of water uptake increases with the increase in concentration of ionized groups. This is due to an increase in repulsion between the ionized groups in the polymer. This allows for a greater amount of swelling of the polymer. The amount of liquid that is absorbed depends partly on the nature of the liquid. The polymer absorbs more pure water than it does solutions. This means that more urine, an aqueous solution, would be absorbed than pure water.

aqueous solution: homogenous mixture in which water is the solvent (primary component)

ionization: dissociation of a molecule into ions carrying + or − charges

New Advances

Diapers continue to become thinner and more absorbent. During the 1990s a modification of the SAP was developed. It uses a surface cross-linker to reduce the "gel block" problem: If the absorbent is saturated with a liquid, it prevents the liquid from moving.

Independent inventors also are continuing to modify the diaper. Marlene Sandberg of Stockholm has constructed a diaper that is 70 percent biodegradable. She uses cornstarch in the preparation of the outer layer of the diaper. This allows her to reduce the amount of polyacrylate used by designing channels in the fill material that help disperse the urine. Other workers in the field dispute that the diaper is 70 percent biodegradable: They say the diapers will not **degrade** that much in a landfill—their ultimate destination.

degrade: to decompose or reduce the complexity of a chemical

Controversy

As with all products, there are advantages and disadvantages to disposable diapers. The new polyacrylate gel has been linked to some side effects, including allergic reactions such as skin irritations, and to toxic shock syndrome. In addition, the dyes in the diapers have been linked to damage of the central nervous system, and disposable diapers may contain low concentrations of dioxin, a by-product of the bleaching process used in the production of the paper pulp found in the absorbent layer. Dioxin has been linked to liver damage and immune system suppression.

Disposables are also considered to be an environmental threat. Only some of the materials used in the diapers are biodegradable (the wood pulp and SAP). The polyethylene and polyester sheets are not biodegradable; neither is the elastic used for better fit, nor the polypropylene used for the tape that is employed as a fastener. Disposable diapers account for up to 2 percent of the total volume of landfills in the United States. The lifetime of the diaper in the landfill depends on several environmental factors: soil condition, groundwater flow, and the presence of other materials in the soil. SEE ALSO MATERIALS SCIENCE; POLYMERS, SYNTHETIC.

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DNA ***See Deoxyribonucleic Acid.***

DNA Replication

Before one cell can divide into two cells, the cell must make a copy of the cellular DNA so that after cell division, each cell will contain a complete complement of the genetic material. Replication is the cellular process by which DNA or the cellular genome is duplicated with almost perfect (and sometimes perfect) fidelity. The replicative process in **prokaryotic** cells, such as *Escherichia coli* (*E. coli*) cells, is best understood and will be described in detail, and the aspects that differ in replicating **eukaryotic cells** will be noted.

prokaryotic: relating to very simple cells of the type found in bacteria

eukaryotic cell: cell characterized by membrane-bound organelles, most notably the nucleus, and that possesses chromosomes whose DNA is associated with proteins

Replication starts by the separation of the strands of DNA and the formation of a local "bubble" at a specific DNA site called the origin of replication (ori). A helicase enzyme uses energy from ATP hydrolysis to effect this action. Single-strand DNA binding proteins stabilize the strands during the subsequent steps. The original DNA strands will function as the templates that will direct **synthesis** of the complementary strands. A nucleotide on the template strand will determine which deoxyribonucleotide (dNTP) will be incorporated in the newly synthesized strand. This replica-

synthesis: combination of starting materials to form a desired product

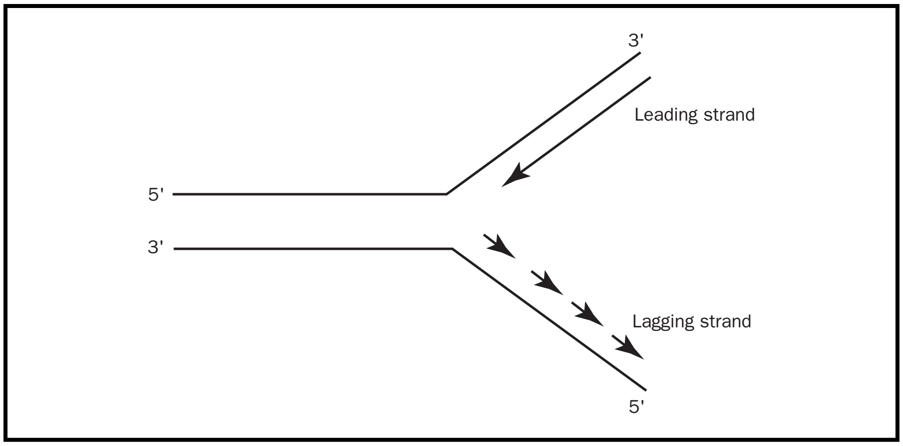

Figure 1. Replication model.

tion model is called semiconservative replication. The opening of the DNA produces two replication forks (see Figure 1), both of which will be the sites for replication. The forks will move in opposite directions relative to the replication machinery, with DNA replication occurring bidirectionally.

To initiate the synthesis of the two strands, a primer strand is needed, which is made by the enzyme primase. This small primer is an **RNA** molecule, which has a **5′-** and a **3′-end**. Replication requires the 3′-hydroxyl group of the deoxyribose. This group is "attacked" by the phosphate of the incoming dNTP, because all DNA polymerases can extend DNA only from the 3′-end (synthesis occurs in the 5′→3′ direction on the primer strand). Because the strands of DNA have opposite orientations, the replication process for each strand is considerably different. Extension of each strand requires very different operations that involve synthesis of a leading strand and a lagging strand. Leading strand synthesis, which progresses toward the fork in a continuous manner, begins with primase synthesizing a short RNA primer at the ori, followed by the action of DNA polymerase III, which incorporates deoxyribonucleotides into the strand, until strand synthesis is complete. If an incorrect nucleotide in incorporated, a proofreading activity in the mechanism removes it and the synthesis continues. Lagging strand synthesis progresses in the direction opposite to fork movement, with the new DNA strand synthesized in 1,000 to 2,000 nucleotide fragments called Okazaki fragments. Each fragment must also be initiated with a primer, followed by synthesis utilizing DNA polymerase III. When the Okazaki fragments are completed, DNA polymerase I both removes the RNA primers and simultaneously replaces the RNA with DNA. This occurs similarly for the single primer on the leading strand. The DNA fragments are then sealed together to produce a continuous strand by the enzyme DNA ligase.

RNA: ribonucleic acid, a natural polymer used to translate genetic information in the nucleus into a template for the construction of proteins

5′ end: situation in nucleic acids in which the phosphate group is attached at the fifth carbon atom from where the base is attached

3′ end: situation in nucleic acids in which the phosphate group is attached at the third carbon atom from where the base is attached

The size of the genomic DNA in eukaryotic cells (such as the cells of yeast, plants, or mammals) is much larger (up to 10^{+11} base pairs) than in *E. coli* (ca. 10^{+6} base pairs). The rate of the **eukaryotic** replication fork movement is about fifty nucleotides per second, which is about ten times slower than in *E. coli*. To complete replication in the relatively short time periods observed, multiple origins of replication are used. In yeast cells, these multiple origins of replication are called autonomous replication sequences (ARSs). As with prokaryotic cells, eukaryotic cells have multiple DNA polymerases. DNA polymerase δ, complexed with a protein called proliferating

eukaryotic: relating to organized cells of the type found in animals and plants

nuclear: having to do with the nucleus of a cell

cell **nuclear** antigen (PCNA), is thought to synthesize the leading strand, whereas DNA polymerase α is the replicase for the lagging strand. Eukaryotic genomes have linear DNA strands and require a special enzyme, called telomerase, to replicate the ends of the chromosomes. SEE ALSO BASE PAIRING; DEOXYRIBONUCLEIC ACID (DNA).

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Dopamine

Dopamine belongs to a family of biological compounds called catecholamines (see Figure 1). Dopamine is synthesized from the compound L-dihydroxyphenylalanine (L-dopa) via the enzyme dopa decarboxylase. In noradrenergic neurons and in the adrenal glands, dopamine is the precursor for the neurotransmitter norepinephrine. In dopaminergic neurons, dopamine itself acts as a neurotransmitter. Although dopaminergic neurons are not as widely distributed in the brain as noradrenergic neurons, they act to coordinate movement, to control the secretion of some hormones, and to regulate mood and emotional stability.

Dopamine's role in the coordination of movement can be partially understood by examining Parkinson's disease. This illness is associated with low levels of dopamine in the brain and is characterized by spastic motion of the eyelids as well as rhythmic tremors of the hands and other parts of the body. One method of treating Parkinson's disease is to increase the concentration of dopamine in the brain. This is most effectively accomplished by administering the precursor of dopamine, L-dopa. In order to prevent concentrations of norepinephrine from increasing as well, L-dopa is given in conjunction with a drug that inhibits norepinephrine **synthesis**.

synthesis: combination of starting materials to form a desired product

The role that dopamine plays in regulating mood and emotional stability can be at least partially grasped by examining dopamine's role in schizophrenia and drug addiction. Schizophrenia is a disorder characterized by delusions, hallucinations, withdrawal from external reality, and emotional unresponsiveness. The dopamine theory of schizophrenia, proposed in 1965, attributes the disorder to elevated brain concentrations of dopamine or to a hypersensitivity of dopaminergic **receptors**, especially the D_2 and D_4 receptor subtypes. Several drugs used to treat schizophrenic patients bind to D_2 and D_4 receptors and block the dopaminergic response.

receptor: area on or near a cell wall that accepts another molecule to allow a change in the cell

amphetamine: class of compounds used to stimulate the central nervous system

Dopamine is also an important component of the brain's "reward system" and is believed to play a role in drug addiction. Increased levels of dopamine have been associated with cocaine, **amphetamine**, and marijuana use, as well as alcohol and nicotine addiction. SEE ALSO NEUROTRANSMITTERS.

Jennifer L. Powers

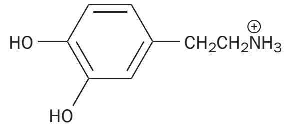

Figure 1. The structure of dopamine as it exists in solution.

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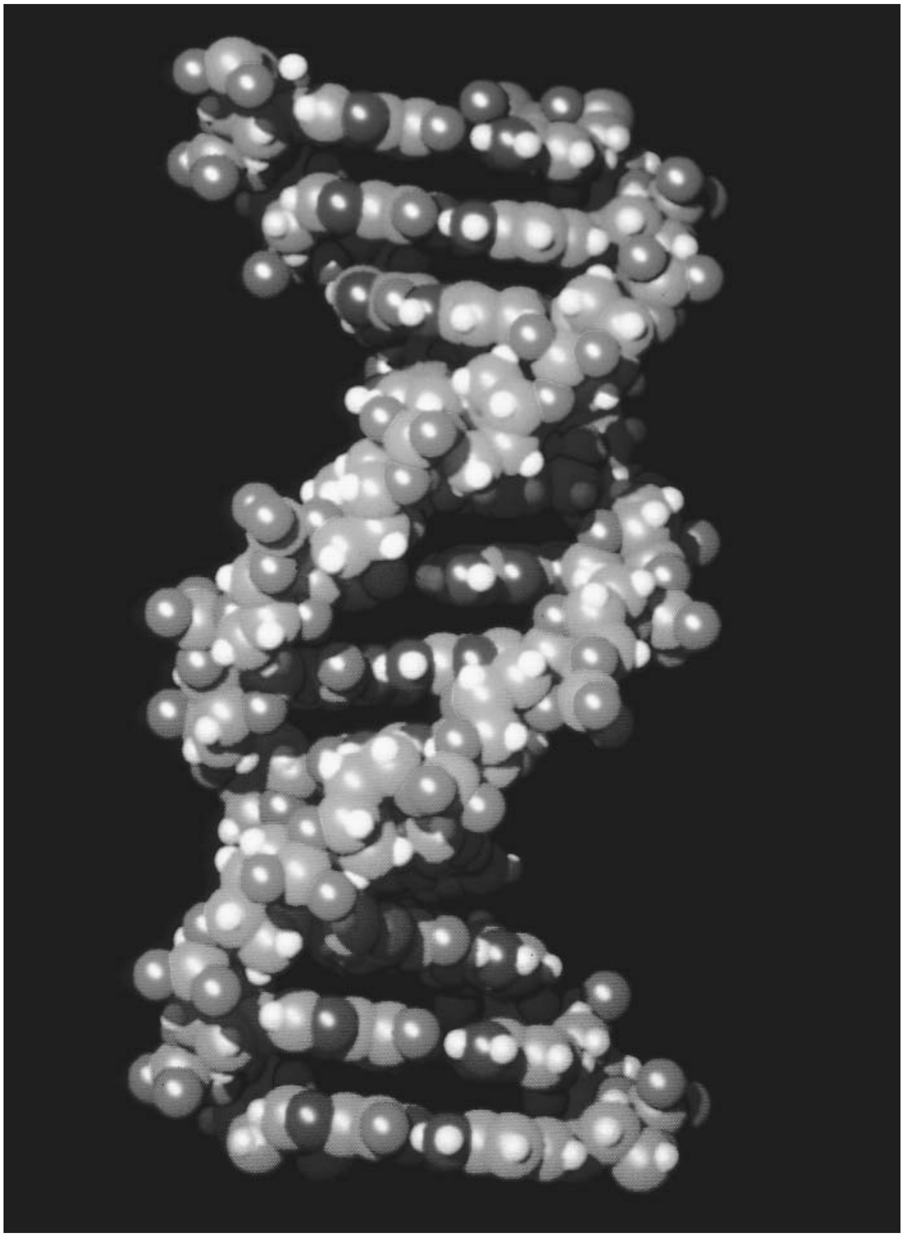
Double Helix

Described in 1953 by James Watson and Francis Crick, the double helix of **DNA** (deoxyribonucleic acid) is the cellular storehouse of genetic information. This biopolymer consists of a pair of complementary chains approximately 2.4 nanometers (9.5×10^{-8} inches) in diameter and composed of

DNA: deoxyribonucleic acid—the natural polymer that stores genetic information in the nucleus of a cell



A computer-generation representation of the double-helix structure of DNA.

deoxyribose sugar molecules linked to each other by phosphoric acid, connecting the number three carbon of one sugar to the number five carbon of another. Attached to each sugar is a heterocyclic base: **adenine**, **guanine**, **cytosine**, or **thymine**. Each turn of the helix contains about 10.4 nucleotides.

These chains are said to be complementary: Guanine on one chain always pairs with cytosine on the opposite strand of DNA by forming three **hydrogen bonds**, and adenine on one chain pairs with thymine on the complementary chain, held in position by two hydrogen bonds. The interchain bonding forms an **attraction** between the two DNA chains and stabilizes the double helix against the strong **repulsive force** of the phosphoric acid residues. The chains are said to be antiparallel; that is, the two chains are held closely together but run in opposite directions, with the **$3'$ end** of one chain matching the **$5'$ end** of the other chain.

DNA performs two important functions. It contains the genetic **code** that provides directions for replication (**synthesis** of new DNA), and thus serves as a storehouse of genetic information, allowing the physical characteristics of parent organisms to be passed on to offspring. DNA also acts as a storehouse of synthetic information. The individual genes can be turned on or off, allowing the information of each codon within a gene to be converted into information contained in messenger RNA (a process known as **transcription**). This information can then be transcribed into protein having **catalytic** or structural properties. SEE ALSO BASE PAIRING; CODON; DNA REPLICATION; HYDROGEN; NUCLEIC ACIDS; WATSON, JAMES DEWEY.

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du Pont, Éleuthère Irénée

FRENCH-AMERICAN INDUSTRIALIST
1771–1834

Éleuthère Irénée du Pont was born in France on June 24, 1771, and died on October 31, 1834, in the United States. He was the son of Pierre du Pont, an active member of the French government in the 1780s and 1790s before, during, and after the French Revolution. In keeping with the spirit of the times, Éleuthère Irénée was named for "liberty and peace." During the rise of Napoléon Bonaparte, Pierre was ordered into exile because of his continuing royalist sympathies. He took his family to the United States, where he later helped negotiate the U.S. purchase of the Louisiana Territory from France.

In 1787 Éleuthère Irénée du Pont worked at Antoine-Laurent Lavoisier's **saltpeter** plant in Essone, France. Here he was exposed to the craft of gunpowder manufacturing and to the application of Lavoisier's new chemistry to an industrial process. When du Pont arrived in the United States in 1800, he began to search for a potentially profitable business op-

CHARGAFF'S RULES

Erwin Chargaff found that the ratios of adenine to thymine and of guanine to cytosine were always 1:1, suggesting that these bases form pairs. The fact that the ratios are 1:1 is referred to as Chargaff's rules.

adenine: one of the purine bases found in nucleic acids, $C_5H_5N_5$

guanine: heterocyclic, purine, amine base found in DNA

cytosine: heterocyclic, pyrimidine, amine base found in DNA

thymine: one of the four bases that make up a DNA molecule

hydrogen bond: interaction between H atoms on one molecule and lone-pair electrons on another molecule that constitutes hydrogen bonding

attraction: force that brings two bodies together, such as two oppositely charged bodies

repulsive force: force that repels two bodies; charges of the same sign repel each other

$3'$ end: situation in nucleic acids in which the phosphate group is attached at the third carbon atom from where the base is attached

$5'$ end: situation in nucleic acids in which the phosphate group is attached at the fifth carbon atom from where the base is attached

code: mechanism to convey information on genes and genetic sequence

synthesis: combination of starting materials to form a desired product

transcription: enzyme-catalyzed assembly of an RNA molecule complementary to a strand of DNA

catalysis: the action or effect of a substance in increasing the rate of a reaction without itself being converted

saltpeter: potassium nitrate; chile saltpeter is sodium nitrate

French industrialist Éleuthère Irénée du Pont, who developed his company into the largest gunpowder manufacturer in the United States.

portunity and soon became aware of the unreliable and generally poor quality of domestic gunpowder at the time. After an unsuccessful attempt to purchase what was then the largest U.S. gunpowder plant located in Frankford, Pennsylvania, he purchased a mill on the Brandywine River in Delaware. This site had the advantage of existing mills with proven water power, nearby access to the port of Wilmington, local willow woods for charcoal, and a community of French-speaking workers. The mills were converted to the manufacture of gunpowder, and by 1811 E.I. du Pont de Nemours & Co. was the country's largest gunpowder manufacturing plant. It became the major supplier of gunpowder during the War of 1812.

On March 19, 1818, an accident at the plant triggered a series of explosions that killed thirty-six workers and destroyed five mill buildings. The company took years to rebuild and recover from this tragedy. In the process of rebuilding, safety became a lasting feature of corporate planning at DuPont. By the time of Éleuthère Irénée's death, DuPont was the primary manufacturer of gunpowder in the United States. As of 2003 it produces much more than gunpowder and is among the largest chemical manufacturers in the world. SEE ALSO LAVOISIER, ANTOINE.

David A. Bassett

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Dyes

The great appeal of textiles lies in their colors and the way that color is used to create patterned effects. Color is applied by the process of dyeing, which in its simplest form involves the immersion of a fabric in a solution of a dyestuff in water. Patterned effects are obtained by selectively applying dyes to fabric, for example by roller printing. The amount of dyestuff required is very small, but its production and application require considerable skill. Changes in the ways of producing dyes during the nineteenth century heralded the modern science-based chemical industry.

Natural Dyes

Dyes obtained from natural products, such as plants and insects, have been used for decorative effect and as symbols of status for thousands of years. The mollusk-derived Roman purple, 6,6′-dibromoindigo, also called Tyrian purple, was remarkable for its fastness to light and washing; it was also an important mark of social distinction. The associated biblical blue holds great religious significance among observant Jews. In China, the emperor and empress wore yellow, the imperial ladies violet, and noblemen of the first grade blue. Explorers of the Americas came across many natural dyes, particularly dyewoods, not previously known in Europe. Native American peoples, such as Navajo and Hopi, were highly skilled dyers. In Europe the blue extracted from the woad plant was used for adornment, through the coloring of skin and later the dyeing of textiles.

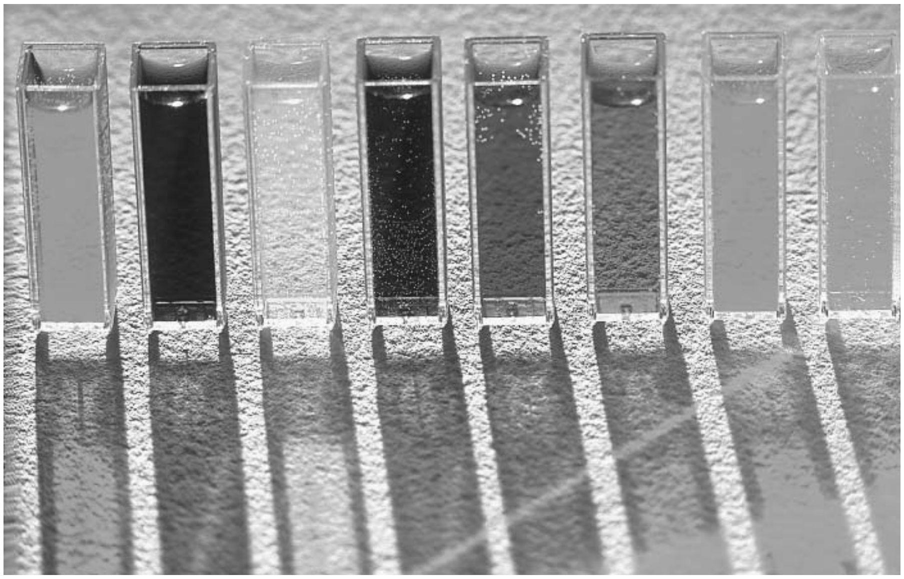
By the sixteenth century dyes played a major role in political and economic history as European nations vied for sources of new colors and the secrets of applying natural colors. *Indigo tinctoria* that yielded a brighter indigo blue than woad arrived in Europe from India and the East. Indigo and the red known as madder, from the roots of the madder plant, were the most important natural dyes. Indigo was used in kimono dyeing in Japan. Madder was the basis of the fiery Turkey red. England's King George II chose indigo for the color of British naval uniforms (hence "navy blue").

Indigo is a vat dye, which means that it was once applied in special vats. It and other vat dyes are insoluble in water. In dyeing, indigo is converted, or reduced, to a white form, which is soluble. Yarn or fabric is then dipped in the vat containing the reduced dye, which on leaving the vat is oxidized in the air back to blue. Tyrian purple and biblical blue are also vat dyes.

Dyes, Industry, and Science

Dyestuffs were central to the first **Industrial Revolution**, from the late eighteenth century, based on the production of and trade in textiles. This

Industrial Revolution: widespread replacement of hand tools by power-driven machines, beginning about 1750 (especially in England)



Containers of fabric dyes.

encouraged chemists to investigate the composition of natural dyes. They extracted the colorant in madder and gave it the scientific name alizarin. Dyes also played a prominent role in the second Industrial Revolution, commencing around 1870, when the quest for synthetic colorants led to the development of science-based industry.

The first of the modern synthetic dyes was invented in London in 1856 by the chemist William Henry Perkin when he was still a teenager. His product was first sold as Tyrian purple, but from 1859 on it was known as mauve, from the French word for the mallow flower. It was made from coal tar, the waste product of the coal gasification process. The coal-tar product benzene was converted in three steps to the dye. Perkin's teacher was the German chemist August Wilhelm Hofmann, who began research to identify the chemical constituents of the new coal-tar or "aniline" dyes. Chemistry in Germany was highly developed at this time, and many Germans journeyed to England to work in the new synthetic dye industry. Starting in the mid-1860s, they returned home, armed with the latest science and technology. The industry soon moved to Germany and Switzerland.

Particularly significant was the production of artificial alizarin red (in 1869), mainly in Germany, and indigo (1897), only in Germany. These synthetic products destroyed the trading monopolies in natural dyes by displacing the large-scale cultivation of madder and indigo. The other new dyes had no analogs in nature. In 1875 the dye chemist Otto N. Witt proposed a theory of color and constitution that is still used to explain how certain arrangements of atoms, called **chromophores**, give rise to color. Other groups called auxochromes enable the bonding to fiber and modify the color.

The development of the synthetic dye industry led to the emergence of classical organic chemistry. Its application in industry was rapid. From the end of the nineteenth century the **intermediates** employed in the manufacture of synthetic dyes were used to make pharmaceutical products such as aspirin. Some synthetic dyes exhibited bactericidal properties; they were called medicinal dyes. **Sulfonamides**, drugs introduced in the 1930s, are based on research into dyestuffs and their intermediates. Less fast dyes have

chromophore: part of the molecule that yields characteristic colors

intermediate: molecule, often short-lived, that occurs while a chemical reaction progresses but is not present when the reaction is complete

sulfonamides: first of a series of drugs used for the prevention and cure of bacterial infections in humans; sulfanomides are amides of sulfuric acids and contain the $-SO_2NRR_1$ group made color photography possible. Indigo is not fast to light and washing, and soon gives a faded effect. Since the 1960s that property has been used to advantage in fashionable denims.

The modern U.S. chemical industry emerged in 1915, when supplies of dyes were cut off by Germany, which required dyes and their intermediates for military purposes, including the manufacture of explosives, and also by the British blockade on German shipping. From the 1970s the by then mature industry declined in Europe and the United States, in part because of environmental difficulties facing dye manufacturers, such as the pollution of surface waters.

Making Colors Last

color fastness: condition characterized by a lack of removal of colored moieties from a base material

Color fastness is important in textiles. It is a measure of how well the dye is attached to fabric (substrate). In the early 1900s a new class of coal-tar dyes, known as the indanthrenes, was invented. Some blue indanthrenes displaced indigo, because they were faster to light and washing, and brighter. The most important of these colorants, collectively known as vat dyes, is vat jade green.

mordant dye: dye substance containing an acidic moiety, e.g., a carboxyl group, which binds metallic compounds, forming insoluble colored compounds

metal: element or other substance the solid phase of which is characterized by high thermal and electrical conductivities

Mordant dyes are those that can be applied only with a fixing agent, or mordant. The fixing agents are often **metal** compounds, particularly those whose cations form coordination complexes. Alizarin is a mordant dye, and with different metal compounds it gives a range of colors. The first synthetic dyes that attached to fabric without the need for a mordant were benzidine dyes, invented in the 1880s. However, early in the twentieth century some of them were found to cause bladder cancer. Their manufacture ceased by the early 1970s. In 1956 chemists at Imperial Chemical Industries (ICI) in England announced the first dyes that bonded chemically to fabric; these fiber-reactive colorants ensured great fastness.

Common Dyes

Fluorescent dyes, or whitening agents, alter the drab gray or yellow appearance of white fabrics that have been washed many times. They do this by absorbing ultraviolet (UV) light and reemitting the absorbed energy as fluorescence in the blue region of the spectrum. This "blueing" makes fabrics look whiter and brighter. Fluorescent dyes are also used as tracers in following sewage and contaminated sources of water, and are important in detection chemistry for drug development.

A wide variety of natural and synthetic dyes are used to color foodstuffs. Florida oranges, often a natural green color when ripe, are sometimes dyed orange with synthetic dyes. Since some synthetic dyes cause illness, their use is restricted, or excluded, even in the coloration of textiles. In the United States, the Pure Food, Drug, and Cosmetic Act enables the Food and Drug Administration (FDA) to control the dyes in foods. This is why these dyes are given names with the prefix FD&C or External D&C.

Hair dyes are of two types: permanent and semipermanent. Permanent dyeing is achieved with a synthetic dye, applied with hydrogen peroxide that first bleaches the natural pigment melanin. Semipermanent dyes are generally made with vegetable extracts, such as henna, that coat rather than penetrate the hair shaft. There are a number of questions about the safety of synthetic hair dyes, since some of the products they contain cause cancer.

TIE-DYEING

Tie-dyeing is, like textile printing, selective dyeing. If a piece of wool is bound tightly with cotton strips and then dyed by immersion in a dye bath, only those areas exposed to the dye will take on its color. After the fabric is removed and allowed to dry, and when the strips of cotton are untied, the tightly bound areas show no color from the dye. Omitting dye from an area creates what is referred to as a reserve. The whole piece can then be placed in a dye bath, so that the reserve areas are now dyed, and the previously dyed areas show the effect of two dyes. This process, called tie-dyeing, creates interesting patterns on fabric and is often used in producing T-shirts, shorts, or handkerchiefs.

Easter egg dyes are natural dyes that can be found around the home. They include blue from cabbage leaves or blueberries, orange from yellow onion skins, red from cranberries or raspberries, pale green from spinach leaves, and light yellow from orange or lemon peels. Dyes often have different colors in acidic and alkaline solutions. This enables them to be used as acid-base indicators. Many dyes are utilized as **biological stains**. SEE ALSO Cosmetics; Perkin, William Henry; Pigments.

biological stain: dye used to provide contrast among and between cellular moieties

Anthony S. Travis

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Dysprosium

66
Dy
DYSPROSIUM
162.50

MELTING POINT: **1,407°C**
BOILING POINT: **2,567°C**
DENSITY: **8,551/kg m^{-3}**
MOST COMMON IONS: **Dy^{4+}, Dy^{3+}, Dy^{2+}**

Dysprosium, taking its name from the Greek word *dysprositos*, meaning "hard to obtain," is a metallic element, discovered, but not isolated, in 1886 in

Paris by the French scientist Paul-Émile Lecoq de Boisbaudran. Its isolation was made possible by the development of ion-exchange separation in the 1950s. Dysprosium belongs to a series of elements called **rare earths**, **lanthanides**, or "4f elements." The occurrence of dysprosium is low: 4.5 ppm (parts per million), that is, 4.5 grams per metric ton in Earth's crust, and 2 x 10^{-7} ppm in seawater. Two minerals that contain many of the rare earth elements (including dysprosium) are commercially important: monazite (found in Australia, Brazil, India, Malaysia, and South Africa) and bastnasite (found in China and the United States). As a **metal**, dysprosium is reactive and yields easily oxides or salts of its triply oxidized form (Dy^{3+} ion).

rare earth elements: older name for the lanthanide series of elements, from lanthanum to lutetium

lanthanides: a family of elements from lanthanum to lutetium having from 1 to 14 4f electrons

metal: element or other substance the solid phase of which is characterized by high thermal and electrical conductivities

Dysprosium or its compounds are used in small quantities in several high-technological applications owing to their thermal, magnetic, and optical properties. For instance, dysprosium is susceptible to large magnetization and is a part of special magnetic **alloys** (e.g., those used for data storage on CDs). A cermet (a combination of a heat resistant ceramic with a metal) of dysprosium oxide and nickel enables the control of **nuclear** reactors, as it easily absorbs neutrons. Dysprosium is put into mercury-vapor lamps and several materials used to generate lasers, to enhance their optical properties. Dysprosium-cadmium chalcogenides are a source of infrared radiation. Some special purpose eyeglasses (e.g., those worn by glassblowers) contain dysprosium. SEE ALSO Cerium; Erbium; Europium, Gadolinium; Holmium; Lanthanides; Lanthanum; Lutetium; Neodymium; Praseodymium; Promethium; Samarium; Terbium; Thulium; Ytterbium.

alloy: mixture of two or more elements, at least one of which is a metal

nuclear: having to do with the nucleus of an atom

Jean-Claude Bünzli

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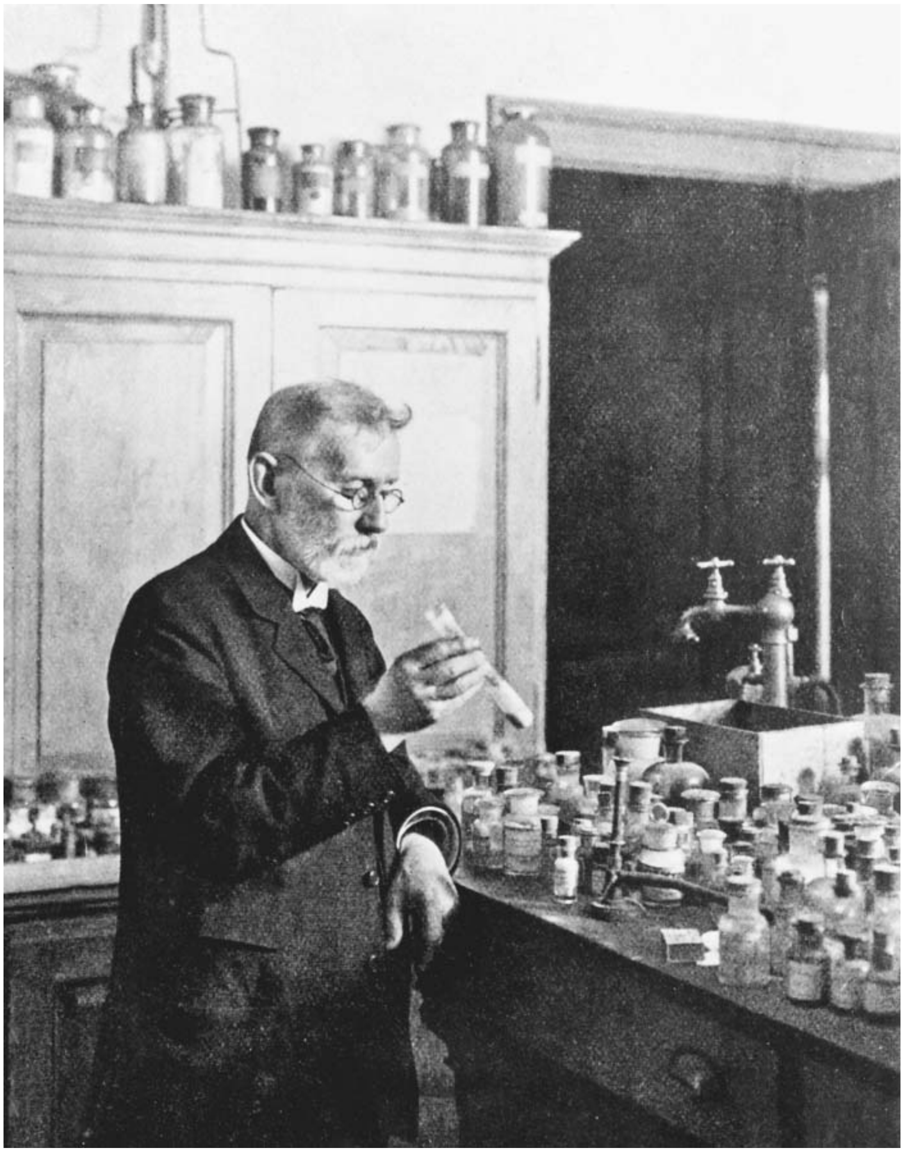
Ehrlich, Paul

GERMAN CHEMIST AND BACTERIOLOGIST
1854–1915

Paul Ehrlich made notable contributions in several areas of medicine including selective dye staining of cells, immunology, cancer research, and chemical therapy of infectious diseases.

Ehrlich was born in Strehlen, Germany, and attended school in Breslau where an older cousin, Carl Weigert, was a physician at a local hospital. Weigert was researching cell staining with synthetic dyes, a procedure that makes cells more visible under a microscope. Weigert demonstrated the technique for his teenage cousin who was immediately fascinated by the process.

As a medical student Ehrlich undertook his own investigations into cell staining techniques, observing that dyes could selectively stain different types of cells. Most of his dyes came from the flourishing German dye industry, and Ehrlich noted that different chemical structures of the dyes gave them different cell staining properties, leading him to the hypothesis that there was a very specific chemical attraction between the dye and certain cells or parts of cells. This concept of specific chemical attractions was to guide much of his life's work.



German chemist and bacteriologist Paul Ehrlich, corecipient, with Ilya Ilyich Mechnikov, of the 1908 Nobel Prize in physiology or medicine, “in recognition of their work on immunity.”

Following graduation from medical school in 1878, Ehrlich accepted a position at a Berlin hospital where he employed his knowledge and skill with synthetic dyes to make numerous important contributions to medicine. He was able to use dyes to differentiate several types of red and white blood cells, including leukemia cells, and to assist German bacteriologist Robert Koch in staining and identifying the tuberculosis bacterium. Cell staining remains in use to identify both healthy and cancerous cells.

In 1883 Ehrlich married a young woman named Hedwig Pinkus, to whom he was quite devoted. They had two daughters, Stephanie and Marianne. In 1888 Ehrlich himself developed tuberculosis, left employment at the hospital, and took a yearlong trip to Egypt where he recovered from the infection.

Ehrlich returned to Berlin in 1889 and established a small research laboratory where he began work on the chemical nature of immunity, antitoxin sera, and the nature of the binding of antibodies to antigens. Over a period of ten years this work led to his concept of complementary chemical binding of antigen to antibody and his famous side chain theory to explain why only part of an antigen was necessary to raise immunity. This work in immunology led to a 1908 Nobel Prize in physiology or medicine.

Ehrlich made significant contributions to understanding cancers, including developing a strain of mouse cancer cells known as Ehrlich ascites cells that are still used in cancer research. Ehrlich's work with the selectivity of staining dyes for specific cells, and the specific binding of one antigen to only one antibody, led to the hypothesis that it should be possible to develop drugs that were so specific to disease cells that they could be considered "magic bullets."

Ehrlich embarked on his search for magic bullets to treat parasitic disease with a vast supply of new chemicals from the German dye industry. In 1909 Ehrlich discovered the first effective cure for syphilis, "compound 606" (also called Salvarsan). For his insight and this achievement Ehrlich is known as the father of chemotherapy. SEE ALSO Dyes.

Robert K. Griffith

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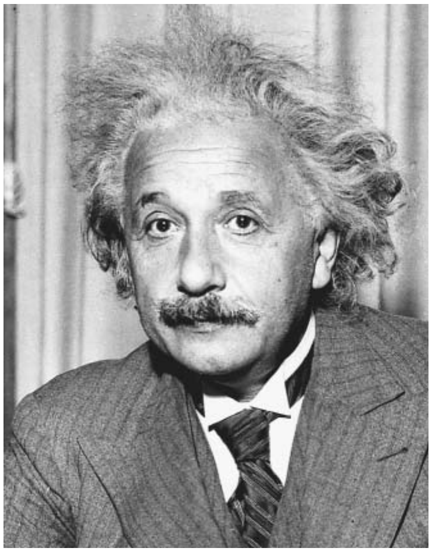
Einstein, Albert

GERMAN-AMERICAN PHYSICIST
1879–1955



American physicist Albert Einstein, recipient of the 1921 Nobel Prize in physics, "for his services to Theoretical Physics, and especially for his discovery of the law of the photoelectric effect."

nuclear: having to do with the nucleus of an atom

For most people asked to name a scientist, "Albert Einstein" is the first name that comes to mind. Einstein's life story, including his difficulties with math in high school, his time spent as a patent clerk in the Swiss Patent Office, his development of the theory of relativity, and his influence on the development of the **nuclear** bomb, is the stuff of legends. Indeed, many a struggling high school science student has sought refuge in the notion that Einstein did not do well in that capacity either.

Einstein is perhaps best known for his work on relativity, and his simple but elegant equation $E = mc^2$, which expresses an equivalence between energy and matter. It is this equation that describes the possibility of the transformation of mass into energy, and the phenomenon that is operational in a nuclear power plant or nuclear bomb. Very little matter can become an inordinate amount of energy, as the speed of light is a constant having an inordinately large value.

What is not so well known about Einstein is that he made contributions to the development of modern chemistry, particularly to the area of quantum mechanics. The Nobel Prize Committee awarded Einstein the Nobel Prize in physics in 1921 "for his services to Theoretical Physics, and especially for his discovery of the law of the photoelectric effect." His explanation of the photoelectric effect helped to validate Planck's view of quantized energy, and has become the basis of the quantitative laws of photochemistry.

The photoelectric effect had been observed as early as 1887, when the physicist Heinrich Hertz noted that light shining on metal decreased the amount of energy or **voltage** needed to eject electrons from the metal's surface. Further studies showed that the kinetic energy of the liberated electrons was independent of the intensity of the light; more light only produced more electrons. This kinetic energy was found to be dependent on wavelength. If the wavelength of the incident light was less than a threshold wavelength, no electrons were observed. Einstein explained the phenomenon in a paper published in the journal *Annalen der Physik* in 1905, the first of four papers by Einstein (all appearing in 1905) that changed science. In essence, Einstein argued that there is an intrinsic "work function" that is required to remove an electron from a metal, a specific amount of energy that depends only on the identity of the metal. The kinetic energy of the released electron is then the difference between the energy supplied by the incoming electromagnetic radiation (including visible light) and the work function. Subsequent experimental verification of Einstein's argument affirmed the claim that light was quantized.

voltage: potential difference expressed in volts

It is one of the ironies of twentieth century science that, although his work on the photoelectric effect helped to advance quantum mechanics, Einstein came to be its chief critic. It was his antagonism toward the probabilistic and nondeterministic nature of quantum phenomena that prompted Einstein to make the often-quoted remark, "I cannot believe that God would choose to play dice with the universe."

Einstein's explanation of the photoelectric effect was not his only contribution to chemistry. His Ph.D. dissertation, submitted in 1905, was entitled "A New Determination of Molecular Dimensions." His investigation of **Brownian motion** (the random movement of microscopic particles suspended in liquids or gases) was intended to establish the existence of atoms as being indispensable to an explanation of the molecular-kinetic theory of heat. And the concept of relativity has shed light on the motions of electrons in the core orbitals of heavy elements. SEE ALSO QUANTUM CHEMISTRY.

Brownian motion: random motion of small particles, such as dust or smoke particles, suspended in a gas or liquid; it is caused by collisions of the particle with gas or solvent molecules that transfer momentum to the particle and cause it to move

Todd W. Whitcombe

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Einsteinium

MELTING POINT: **1,133K**
BOILING POINT: **1,269K**
DENSITY: **8.8 +/- g/cc**
MOST COMMON IONS: **Es^{3+}, Es^{2+}**

99
Es
EINSTEINIUM
252

Einsteinium, the tenth member of the actinide series, was discovered in 1952. Einsteinium and fermium (element 100) were most unexpectedly produced in the explosion of the first U.S. thermonuclear device, "Mike," tested at Eniwetok Atoll in the Pacific Ocean on November 1, 1952. Early analyses of debris from that explosion indicated that something unusual had occurred; the new, very neutron-rich **isotope** of plutonium, ^{244}Pu, was found during mass spectrometric analyses performed at the Argonne National Laboratory and another isotope of plutonium, ^{246}Pu, was detected at the Los Alamos Scientific Laboratory in the course of analyses of the Pu fractions. Scientists at the Radiation Laboratory at the University of California, Berkeley, using their previous experience with the separation of individual actinide elements, then joined in the search for trans-californium elements (elements of higher **atomic number** than californium). Tons of coral from the atoll were laboriously processed, and ^{253}99 (half-life 20 days) and ^{255}100 (half-life 20 hours) were positively identified based on the order of their elution (removal) from a cation-exchange resin column with an α-hydroxyisobutyrate solution. Because of the huge, nearly instantaneous neutron flux generated in the explosion, at least seventeen neutrons were successively captured by the ^{238}U in the thermonuclear device, producing uranium isotopes through ^{255}U, many of which β-decayed to higher atomic number elements, thus producing ^{253}Es and ^{255}Fm. After their declassification, these results were published jointly by the Berkeley Radiation Laboratory, the Argonne National Laboratory, and the Los Alamos Scientific Laboratory (Ghiorso et al., p. 1048[L], 1955).

isotope: form of an atom that differs by the number of neutrons in the nucleus

atomic number: the number of protons in an atomic nucleus, expressed in terms of electric charge; it is usually denoted by the symbol Z

The name einsteinium was chosen for element 99, in honor of the great scientist Albert Einstein. Einsteinium isotopes of masses 241 through 256 are known. All are radioactive, decaying by **α-particle** emission, electron capture, spontaneous **fission**, and β-decay. The mass 241 isotope has the shortest half-life (8 seconds), and the mass 252 isotope has the longest (1.29 years). The ground state electronic configuration of the gaseous einsteinium atom is [Rn]5f^{11}7s^2, analogous to that of its **lanthanide** homologue (holmium). The most stable ion in **aqueous solution** is Es^{3+}, but Es^{2+} and Es^{4+} have been reported, and the **metal** is divalent. SEE ALSO ACTINIUM; BERKELIUM; EINSTEIN, ALBERT; FERMIUM; LAWRENCIUM; MENDELEVIUM; NEPTUNIUM; NOBELIUM; PLUTONIUM; PROTACTINIUM; RADIOACTIVITY; RUTHERFORDIUM; THORIUM; TRANSMUTATION; URANIUM.

α-particle: subatomic particle with 2+ charge and mass of 4; a He nucleus

fission: process of splitting an atom into smaller pieces

lanthanides: a family of elements from lanthanum to lutetium having from 1 to 14 4f electrons

aqueous solution: homogenous mixture in which water is the solvent (primary component)

metal: element or other substance the solid phase of which is characterized by high thermal and electrical conductivities

Darleane C. Hoffman

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Elastomer ***See Rubber.***

Electrochemistry

Electrochemistry deals with the links between chemical reactions and electricity. This includes the study of chemical changes caused by the passage of an electric current across a medium, as well as the production of electric energy by chemical reactions. Electrochemistry also embraces the study of **electrolyte solutions** and the chemical equilibria that occur in them.

electrolyte solution: a liquid mixture containing dissolved ions

Many chemical reactions require the input of energy. Such reactions can be carried out at the surfaces of electrodes in cells connected to external power supplies. These reactions provide information about the nature and properties of the chemical species contained in the cells, and can also be used to synthesize new chemicals. The production of chlorine and aluminum and the electroplating and electrowinning of **metals** are examples of industrial electrochemical processes. Electrochemical cells that produce electric energy from chemical energy are the basis of primary and secondary (storage) batteries and fuel cells. Other electrical phenomena of interest in chemical systems include the behavior of ionic solutions and the conduction of current through these solutions, the separation of ions by an electric field (**electrophoresis**), the corrosion and passivation of metals, electrical effects in biological systems (bioelectrochemistry), and the effect of light on electrochemical cells (photoelectrochemistry).

metal: element or other substance the solid phase of which is characterized by high thermal and electrical conductivities

electrophoresis: migration of charged particles under the influence of an electric field, usually in solution; cations, positively charged species, will move toward the negative pole and anions, the negatively charged species, will move toward the positive pole

Electrochemical Cells

An electrochemical cell generally consists of two half-cells, each containing an electrode in contact with an electrolyte. The electrode is an electronic conductor (such as a metal or carbon) or a semiconductor. Current flows through the electrodes via the movement of electrons. An electrolyte is a **phase** in which charge is carried by ions. For example, a solution of table salt (sodium chloride, NaCl) in water is an electrolyte containing sodium cations (Na^+) and chloride **anions** (Cl^-). When an electric field is applied across this solution, the ions move: Na^+ toward the negative side of the field and Cl^- toward the positive side.

phase: homogeneous state of matter

anion: negatively charged chemical unit, like Cl^-, CO_3^{2-}, or NO_3^-

The half-cells are connected by a cell separator that allows ions to move between the half-cells but prevents mixing of the electrolytes. The separator can consist of a salt bridge, or tube of **aqueous solution** plugged at both ends with glass wool, or it can be an ion exchange membrane or a sintered-glass disk. In some cases both half-cells use the same electrolyte, so that the electrochemical cell consists of two electrodes in contact with a single electrolyte. Electrochemical cells are usually classified as either **galvanic** or electrolytic. In galvanic cells, reactions occur spontaneously at the electrode–electrolyte interfaces when the two electrodes are connected by a conductor such as a metal wire. Galvanic cells convert chemical energy to electric energy and are the components of batteries, which usually contain several cells connected in series. In electrolytic cells, reactions are forced to occur at the electrode–electrolyte interfaces by way of an external source of power connected to both electrodes. Electric energy from the external source is converted to chemical energy in the form of the products of the electrode reactions.

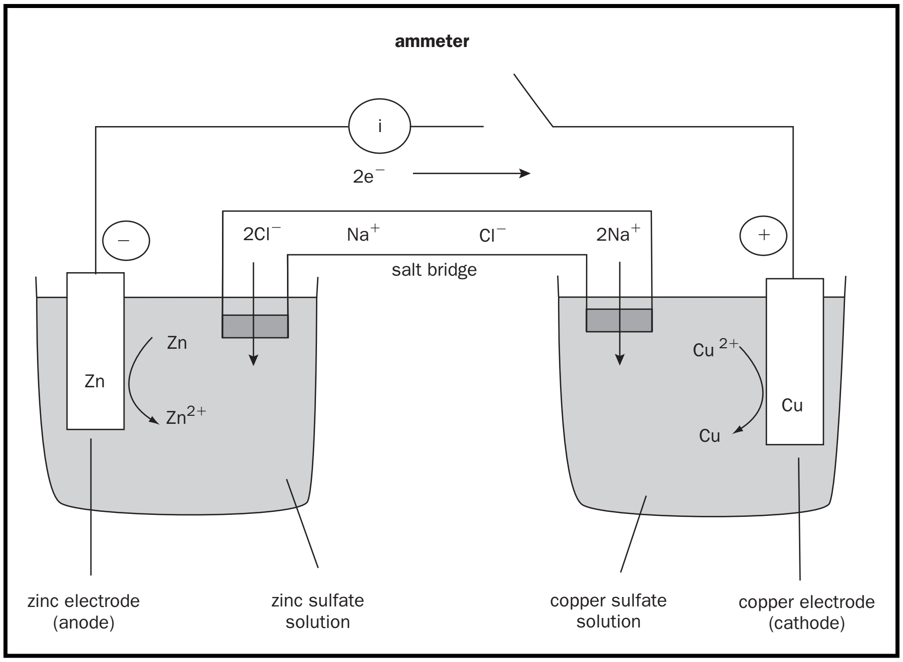
aqueous solution: homogenous mixture in which water is the solvent (primary component)

galvanic: relating to direct current electricity especially when produced chemically

The galvanic cell shown in Figure 1 is known as the Daniell cell and was used as an early source of energy. It consists of a zinc (Zn) electrode in contact with an aqueous zinc sulfate solution and a copper (Cu) electrode in contact with an aqueous copper sulfate solution. When the external switch is closed, an atom of zinc on the zinc electrode is oxidized to zinc ion, liberating two electrons.

$$Zn \rightarrow Zn^{2+} + 2e^- \tag{1}$$

Figure 1. Daniell Cell.



The electrons pass through the external wire and reduce a copper ion to an atom of copper metal on the surface of the copper electrode.

$$Cu^{2+} + 2e^- \rightarrow Cu \qquad (2)$$

The electron flow in the external circuit represents an electric current produced by the cell. Ions flow within the electrolytes and across the salt bridge, as shown in the figure, to prevent an imbalance of ionic charge in the solutions that could result from the occurrence of these two electrode reactions. The overall cell reaction is the reduction of copper ion by zinc.

$$Cu^{2+} + Zn \rightarrow Cu + Zn^{2+} \qquad (3)$$

brine: water containing a large concentration of salts, especially sodium chloride (NaCl)

The electrolytic cell shown in Figure 2 is the industrial chloralkali cell in which **brine** (an aqueous sodium chloride solution) is electrolytically converted to chlorine and caustic soda (sodium hydroxide, NaOH). The external power source supplies electric energy to drive the overall reaction.

$$2Cl^- + 2H_2O \rightarrow Cl_2 + H_2 + 2OH^- \qquad (4)$$

Chloride ion is oxidized to chlorine gas at the carbon electrode, and water is reduced to hydrogen gas (H_2) and hydroxide ion (OH^-) at the iron electrode. The electrolytes are maintained as electrically neutral by a flow of sodium ions through the separator (such as an ion exchange membrane).

oxidation: process that involves the loss of electrons (or the addition of an oxygen atom)

The electrode where **oxidation** occurs, the zinc electrode in Figure 1 and the carbon electrode in Figure 2, is called the anode, while the electrode where reduction occurs is called the cathode. Reactions (1) and (2) are known as half-reactions, whereas reactions (3) and (4) are called oxidation-reduction (redox) reactions.

Electrode Potentials

voltage: potential difference expressed in volts

Current and potential (or **voltage**) are the two electrical variables of greatest interest in electrochemical cells. Current is related to the rate of the elec-

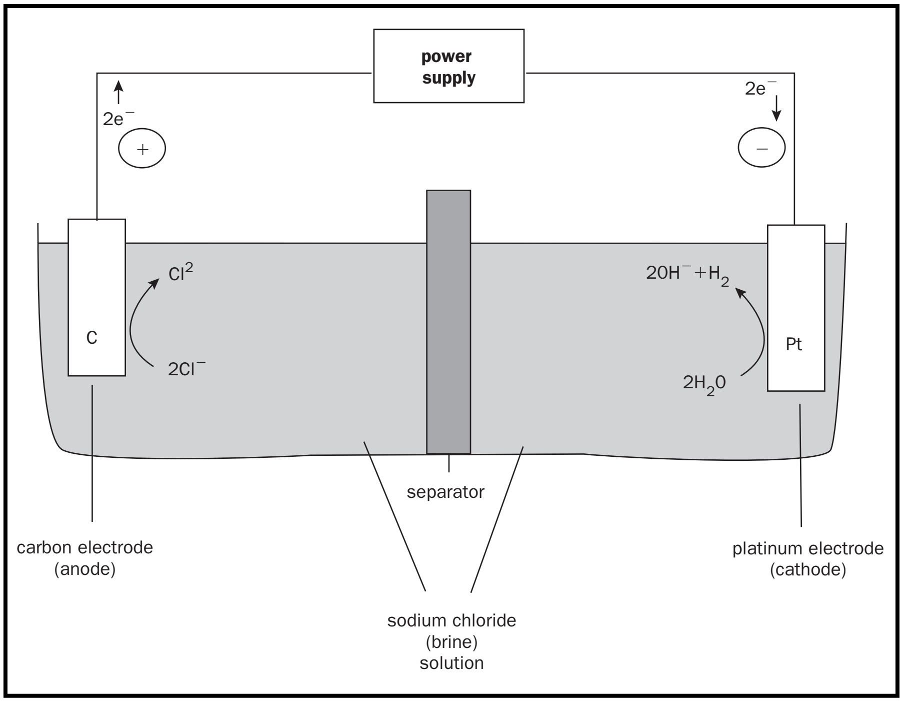


Figure 2. Electrolytic Cell.

trode reactions, and the potential, to the cell energetics. Current is measured in amperes (A), or the amount of electricity in coulombs (C) that passes across a medium per second(s). Potential between the two electrodes is measured in volts (V) with a voltmeter. Potential (V) has units of energy or work (joules, J) per amount of electric charge (C). That is, 1 V = 1 J/C, so that the cell potential is a measure of the energy of the cell reaction. The cell is said to be at open circuit when no current flows; that is, when there are no external connections to the electrodes. Under these conditions, no electrode reactions occur.

Measurements of the potentials of galvanic cells at open circuit give information about the thermodynamics of cells and cell reactions. For example, the potential of the cell in Figure 1, when the solution concentrations are 1 molar (1 *M*) at 25°C, is 1.10 V. This is called the standard potential of the cell and is represented by E°. The available energy (the Gibb's free energy $\Delta G°$) of the cell reaction given in equation (3) is related to E° by

$$\Delta G° = -nFE° \tag{5}$$

where n is the number of electrons transferred in the reaction (in this case two) and F is a proportionality constant, called the Faraday (96,485 coulombs/equivalent). The cell potential is the difference in potential of the two half-cells. Tables of standard electrode potentials of half-reactions have been compiled; representative values are given in Table 1. These are frequently tabulated with respect to the standard or normal hydrogen electrode (SHE or NHE), which is arbitrarily assigned a half-cell potential of zero. Thus the value, +0.34 V, is assigned to the half-reaction $Cu^{2+} + 2e^- \rightarrow Cu$ and

$$E° = +0.34 \text{ V vs NHE} \tag{6}$$

Similarly, the standard potential for the Zn/Zn^{2+} cell yields $Zn^{2+} + 2e^- \rightarrow Zn$ and

Table 1.

REPRESENTATIVE STANDARD POTENTIALS

Half Reaction	E^o vs NHE
$Li^+ + e^- \rightarrow Li$	−3.045
$Mg^{2+} + 2e^- \rightarrow Mg$	−2.356
$Al^{3+} + 3e^- \rightarrow Al$	−1.67
$Zn^{2+} + 2e^- \rightarrow Zn$	−0.7626
$Cr^{3+} + e^- \rightarrow Cr^{2+}$	−0.424
$2H^+ + 2e^- \rightarrow H_2$	0.000
$Cu^{2+} + 2e^- \rightarrow Cu$	0.340
$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$	1.229
$F_2 + 2e^- \rightarrow 2F^-$	2.87

SOURCE: Bard, Allen J. et al., eds. (1985). *Standard Potentials in Aqueous Solutions.* New York: Marcel Dekker.

$$E^\circ = -0.76 \text{ V vs NHE} \tag{7}$$

The difference between these two half-cell potentials yields the standard potential of the Zn-Cu cell.

The standard potential applies to a half-cell when all the reactants are present at unit activity; that is, when the solution species are near a concentration of 1 molar. The actual half-cell potential *E* is a function of the solution concentrations and is related to these and to the standard potential E° by the Nernst equation. The Nernst equation for the generalized half-reaction

$$\text{Oxidized Species} + ne^- \rightarrow \text{Reduced Species} \tag{8}$$

is

$$E = E^\circ + \frac{RT}{nF} \ln \frac{[\text{Oxidized Species}]}{[\text{Reduced Species}]} \tag{9}$$

where *R* is the universal gas constant, *T* is the temperature on the Kelvin (absolute) scale, and the terms [Oxidized Species] and [Reduced Species] denote the activities of the species in the half-cells. The activities of pure solids and liquids are taken as unity. At 25°C, $(RT/F) = 0.025$ V.

Common Batteries

In most flashlights, toys, and remote controllers for televisions, primary batteries are used. The cell reactions in primary batteries are irreversible. During use, reactants are converted to products, and when the reactants are used up, the battery is "dead." The inexpensive flashlight batteries sold in retail stores use a design called a Leclanche dry cell. The body of the battery is made of zinc, which acts as the anode. A carbon rod in the center of the cell serves as the cathode. It is surrounded by a moist paste of graphite powder (carbon), manganese dioxide (MnO_2), and ammonium chloride (NH_4Cl). The anode reaction is the oxidation of the zinc cylinder to zinc ions. The cathode reaction involves the reduction of manganese dioxide. A simplified version of the overall reaction is

$$Zn + 2MnO_2 + H_2O \rightarrow Zn^{2+} + Mn_2O_3 + 2OH^- \tag{10}$$

Alkaline cells are similar, except that the zinc case is porous and the paste around the carbon cathode is moist manganese dioxide and potassium hydroxide. These are more expensive than ordinary zinc-carbon cells, but they maintain a high voltage longer.

The lead-acid storage battery used in automobiles is a secondary battery; it is rechargeable. That is, the automobile battery operates as a galvanic cell when used to start the engine (when discharging), and as an electrolytic cell when it is charged by the alternator or by an external battery charger. The anode consists of porous lead plates in contact with a sulfuric acid (H_2SO_4) solution. The cathode consists of lead dioxide (PbO_2) plates, also in sulfuric acid. Electrons flow from the lead plates to the lead oxide plates. As lead (Pb) loses electrons, it forms lead ions (Pb^{2+}) that react with sulfate ions ($SO_4{}^{2-}$) in solution to form insoluble lead sulfate ($PbSO_4$). When PbO_2 gains electrons, it too reacts with $SO_4{}^{2-}$ ions in solution to form solid $PbSO_4$. The cell reaction is

$$\mathrm{Pb} + \mathrm{PbO_2} + 4\mathrm{H^+} + 2\ \mathrm{SO_4{}^{2-}} \rightarrow 2\mathrm{PbSO_4} + 2\mathrm{H_2O} \qquad (11)$$

and proceeds from left to right when the battery is discharging and from right to left when charging.

The rechargeable nickel-cadmium (Ni-Cad) batteries are used in a variety of cordless appliances such as telephones, battery operated tools, and portable computers. During discharge, cadmium metal (Cd) acts as the anode, and nickel dioxide (NiO_2) as the cathode. Both metals form insoluble hydroxides due to the presence of the potassium hydroxide electrolyte. The cell reaction during discharge is

$$\mathrm{NiO_2} + \mathrm{Cd} + 2\mathrm{H_2O} \rightarrow \mathrm{Ni(OH)_2} + \mathrm{Cd(OH)_2} \qquad (12)$$

The reaction is reversed during charging. SEE ALSO ALUMINUM; FARADAY, MICHAEL.

Cynthia G. Zoski

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Electronic Materials *See Semiconductors.*

Elion, Gertrude Belle

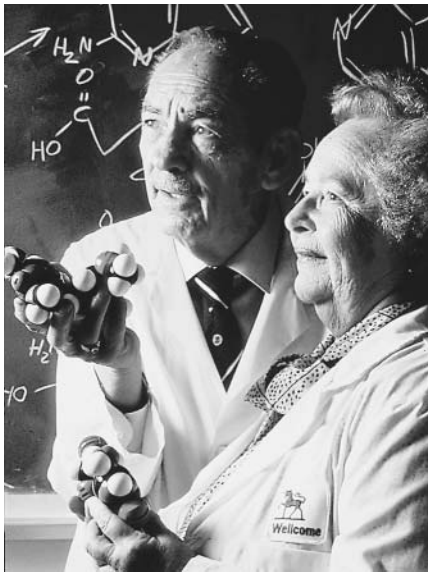
AMERICAN CHEMIST AND MEDICAL RESEARCHER
1918–1999

The Nobel Prize Committee rarely honors the work of scientists who develop new drugs. However in 1988, in awarding the Nobel Prize in physiology or medicine to Gertrude Elion and her colleague at the Burroughs

Wellcome Pharmaceutical Laboratories, George Hitchings, it recognized the work of this pair that led to the development of a series of important drugs, among these drugs used to treat malaria, the leukemias, viral infections, and some forms of impaired immune response.

Born on January 23, 1918, in New York City, Gertrude Elion graduated from Hunter College, in New York, in 1937 with an A.B. degree in chemistry. Unsuccessful in her efforts to enroll in graduate school, she worked for several years in pharmaceutical companies and as a teacher in New York City high schools while continuing her education part time. She earned an M.S. degree from New York University in 1941.

In 1944 Elion joined the Wellcome Research Laboratories, a subdivision of Burroughs Wellcome, as a senior research chemist; by 1967 she was head of their experimental therapy section. Probably the only woman to hold a top-ranking position in a major pharmaceutical company, in 1967 and for many years after, she is said to have felt that she experienced no discrimination at Burroughs Wellcome.



American chemist Gertrude B. Elion (right) with her colleague George H. Hitchings, recipients, with Sir James W. Black, of the 1988 Nobel Prize in physiology or medicine, "for their discoveries of important principles for drug treatment."

metabolism: all of the biochemical processes that take place within living organisms; comprises processes that produce complex substances from simpler components, with a consequent use of energy (anabolism), and those that break down complex food molecules, thus liberating energy (catabolism)

DNA: deoxyribonucleic acid—the natural polymer that stores genetic information in the nucleus of a cell

adenine: one of the purine bases found in nucleic acids, $C_5H_5N_5$

cytosine: heterocyclic, pyrimidine, amine base found in DNA

guanine: heterocyclic, purine, amine base found in DNA

thymine: one of the four bases that make up a DNA molecule

synthesis: combination of starting materials to form a desired product

Her early work focused on the **metabolism** of nucleic acids. In 1944 little was known about these compounds beyond the fact that deoxyribonucleic acid (**DNA**) is the main component of the cell nucleus, and that DNA is composed of repeating units, called nucleotides, whose structures incorporate heterocyclic bases (that is, organic compounds with rings containing nitrogen atoms; the four bases involved are **adenine**, **cytosine**, **guanine**, and **thymine**). Elion's hope was that an understanding of the **synthesis** of nucleic acids in normal cells (and eventual comparisons with nucleic acid synthesis in malignant cells and in disease-causing microorganisms) would suggest ways to block selectively the metabolism of cancer cells or of pathogens without harming normal cells. She therefore proceeded to synthesize a number of compounds that resembled and that might mimic the substance used in DNA synthesis and in this way might block the formation of DNA in harmful cells.

Working with 2,6-diaminopurine (2,6-DAP), a derivative of adenine, Elion found that it inhibited nucleic acid synthesis in cancer cells and was effective in treating mouse leukemia. During the early 1950s, following the elucidation of the structure of DNA, interest in nucleic acid metabolism became intensified, and scientists investigating it, including Elion and her group, found themselves at the forefront of biochemical research. Elion synthesized 6-mercaptopurine (6-MP), another derivative of adenine, which also inhibited DNA synthesis. It was approved by the U.S. Food and Drug Administration in 1953 for the treatment of acute childhood leukemia. Its success led her to probe its exact mode of action using newly developed radiochemical techniques, a breakthrough in drug-related research that advanced considerably the rational design of therapeutic agents. Elion studied 6-MP as a possible inhibitor of antibody-forming cells. As a result, its derivative Imuran (azathioprine) has been used as an antirejection drug in kidney transplants.

Other notable research by Elion led to the development of the antiviral drug Acyclovir (acycloguanosine), which has been used to treat the herpes simplex viruses. Her studies during the 1970s showed that Acyclovir inhibited viral replication by interfering with viral DNA synthesis. The subsequent development of AZT (azidothymidine), which works in much the same way as Acyclovir against the human immunodeficiency virus (HIV), was carried out at Burroughs Wellcome after Elion retired in 1983 (although she worked after 1983 as a consultant).

In addition to the 1988 Nobel Prize (which she shared with Hitchings and British scientist Sir James Black), Elion received other awards and several honorary doctorates. Active in public service, she served on both national and international health committees. She died on February 20, 1999, in Chapel Hill, North Carolina. SEE ALSO DEOXYRIBONUCLEIC ACID (DNA); DNA REPLICATION; NUCLEIC ACIDS; NUCLEOTIDE.

Mary R. S. Creese

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Endorphins

Endorphins are small **neuropeptides** that are produced by the body and act to reduce pain—hence, the name endorphin (a shortened version of endogenous morphine). The term "enkephalin" (meaning literally "in the head") is also applied to endorphins, but usually refers to smaller molecules that have pain-relieving properties.

neuropeptide: neurotransmitter released into the bloodstream via nerve cells

Endorphins were discovered when scientists found sites where molecules such as morphine bind to nerve cells and reasoned that the body must use these sites to bind chemical compounds. Experiments showed that the compounds were small peptides, and the actions of endorphins were determined by a number of researchers.

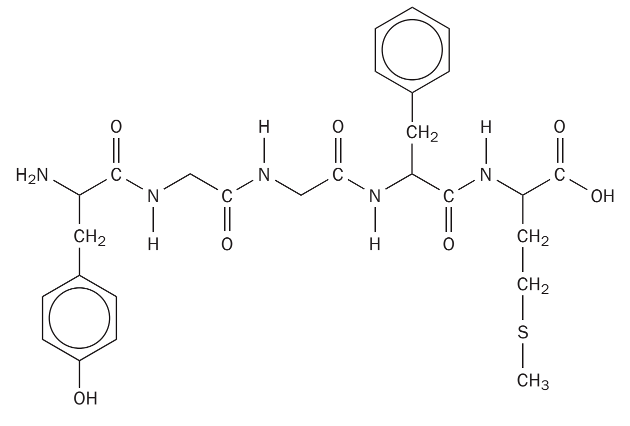
Although similar in primary structure to proteins, endorphins are smaller, ranging from five to forty or more amino acids in length. Endorphins are not considered to be neurotransmitter molecules, but are instead classified as neuromodulatory, that is, they modify the action of neurotransmitters through a number of effects associated with pain or pleasure.

Protein molecules are often synthesized in long chains by the body and cut apart to form functional individual protein units. β-endorphin molecules are produced by the body as portions of larger proopiomelanocortin (POMC) molecules, which are **coded** for by a single gene, synthesized as large molecules, and then cut by enzymes into active subunits. POMC also contains several hormones. The β-endorphin molecules function to relieve pain or produce pleasurable feelings and contain within their structure the pentapeptides met-enkephalin and leu-enkephalin. Composed of five amino acids joined by amide linkages, met-enkephalin (see Figure 1) and leu-enkephalin (see Figure 2) differ only in the amino acid present at the **carboxylic acid** (C-terminal) end.

code: mechanism to convey information on genes and genetic sequence

carboxylic acid: one of the characteristic groups of atoms in organic compounds that undergoes characteristic reactions, generally irrespective of where it occurs in the molecule; the $-CO_2H$ functional group

Figure 1. Met-enkephalin



Tyrosine—Glycine—Glycine—Phenylalanine—Methionine—COOH
(Met-enkephalin)

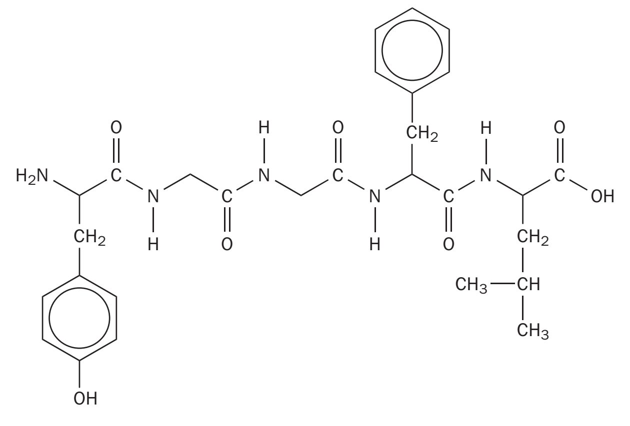
neurologic: of or pertaining to the nervous system

analgesic: compound that relieves pain, e.g., aspirin

receptor: area on or near a cell wall that accepts another molecule to allow a change in the cell

A wide range of physiological effects has been observed for endorphins, but the ultimate function and number of endorphins may not yet be known. Endorphins exhibit a number of **neurological** effects associated with the relief of pain. The administration of exogenous endorphins (those prepared outside the body) stimulates the release of many other hormones including prolactin, adrenocorticotropic hormone (ACTH), and antidiuretic hormone. The **analgesic** effects of morphine are commonly believed to be caused by binding to **receptor** sites for endorphins, but few beneficial effects of treatment with exogenous endorphins have been reported.

Early speculations concerning the function of endorphins suggested that they were natural painkillers that the body produced to alleviate pain in circumstances requiring an individual to continue functioning in spite of injury or stress. Examples of such situations might include childbirth, exercise, and combat. In addition to affecting one's perception of pain, endorphins may be involved in other phenomena such as runner's high and acupuncture. Persons who exercise regularly have higher than usual amounts of β-



Tyrosine—Glycine—Glycine—Phenylalanine—Leucine—COOH
(Leu-enkephalin)

Figure 2. Leu-enkephalin

endorphin in their bloodstream, and the levels of β-endorphin molecules increase during exercise, perhaps accounting for the enhanced feelings of well-being experienced by long-distance runners. Acupuncturists insert and manipulate long needles at precise locations on the skin. After insertion of the needles, patients experience a reduction in pain or may have other physiological responses. In some cases, the stimulation of these acupuncture points by massage may result in the release of endorphins into the blood. Practices such as squeezing the upper lip to stifle a sneeze or massaging the fleshy area between the thumb and forefinger to alleviate a headache may be related to endorphin effects.

Healthy humans are able to overcome stress and pain, allowing them to continue functioning without being overcome by either. To some degree the response is probably psychological, but evidence that the endorphin effect is real exists in the relationship of the opioid-like drug naloxone to the placebo effect. Given a placebo (a so-called sugar pill), many patients report a decrease in pain. The placebo effect is reduced if naloxone, a drug used to treat the intoxicating effects of narcotics, is administered. The administration of naloxone also reduces the endorphin effect; if given naloxone, patients report increased sensitivity to pain. In addition, abnormal levels of endorphins may be associated with mental illness such as autism or depression. For example, an autistic patient might produce so much endogenous endorphin that he or she does not need to react to the world outside, and a depressed person might not produce enough endorphin to withstand the pain and pressures of daily life. SEE ALSO NEUROTRANSMITTERS; PEPTIDE BOND.

Dan M. Sullivan

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Energy

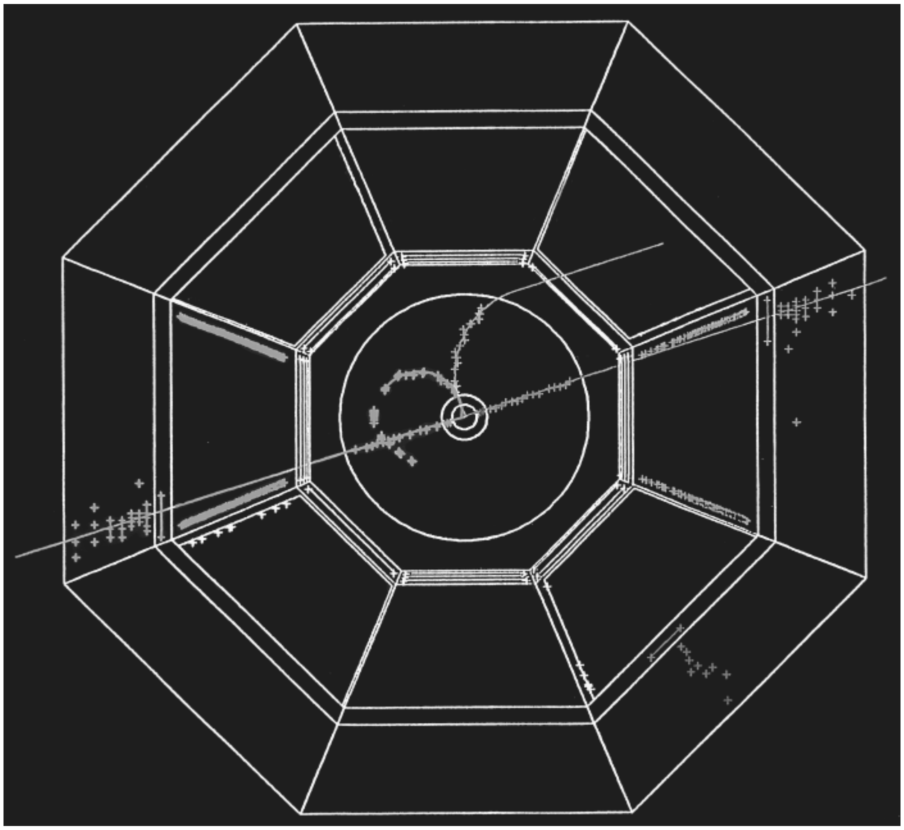
In the discussion of energy, the fundamental concept is that of work, which is motion against an opposing force. Energy is the capacity to do work. An object traveling at high speed and impacting on another object can do more work—can drive the object farther against an opposing force—than the same object moving slowly. This contribution to energy, the energy ascribed to motion, is called kinetic energy. The kinetic energy of an object of mass m traveling at a speed v is $\frac{1}{2}mv^2$. An object may also have energy by virtue of its position. An object high above the surface of Earth has more energy (can do more work) than one at its surface. This contribution to the total energy, the energy due to position, is called potential energy. The relation between the object's position and potential energy depends on the nature of the force field it experiences. The potential energy of a body of mass m at a height h above the surface of Earth is mgh, where g is the acceleration of free fall at the location. More important for chemistry is the potential energy of one charge near another charge. The Coulomb potential energy of a charge q_1 at a distance r from a charge q_2 is given by $q_1q_2/4\pi\epsilon_0 r$, where ϵ_0 is a fundamental constant called the vacuum permittivity. Energy is also stored in the electromagnetic field in the form of photons. The energy of a **photon** of radiation of frequency v is hv, where h is Planck's constant.

photon: a quantum of electromagnetic energy

Energy is conserved. That is, the sum of the kinetic and potential energies of a single body remains constant provided it is free of external influences (forces). Thus, a falling weight accelerates: The fall implies a reduction of potential energy and the acceleration implies an increase in kinetic energy; the sum, though, is constant. A generalization (which can be interpreted as an implication) of the conservation of energy is the first law of thermodynamics, which focuses on a property of a many-body system called the internal energy. The internal energy can be interpreted as the sum of all the kinetic and potential energies of all the particles comprising the system. The first law of thermodynamics states that the internal energy of an isolated system is constant. The first law is closely related to the conservation of energy, but it acknowledges the possibility of the transfer of energy as heat, which is outside the reach of mechanics itself.

The special theory of relativity states that the mass of a body is a measure of its energy: $E = mc^2$, where c is the speed of light. That is, energy and mass are equivalent and interconvertible. Changes in mass are measurable only when changes in energy are considerable, which in practice commonly means for **nuclear** processes.

nuclear: having to do with the nucleus of an atom



An electronic display of the decay of an upsilon particle in a CLEO detector.

In chemistry we are often concerned with the transfer of energy from one location (e.g., a reaction vessel) to another (the surroundings of that vessel). One mode of transfer is by doing work. For example, work is performed when gases evolved in a reaction push back a movable wall (e.g., a piston) against an opposing force, such as that due to the external atmosphere or a weight to which the piston is attached. Another mode of transfer is as heat. Heat is the transfer of energy that occurs as a result of a temperature difference between a system and its surroundings when the two are separated by a diathermic wall (a wall that allows the passage of energy as heat). A metal wall is diathermic, a thermally insulated wall is not diathermic. Finally, energy may leave a system as electromagnetic radiation, for example as in chemiluminescence—the emission of radiation from matter in energetically excited molecular states produced in the course of a chemical reaction, and as a result of **spectroscopic** transitions. We shall concentrate on the first two modes of transfer, work and heat.

spectroscopy: use of electromagnetic radiation to analyze the chemical composition of materials

At a molecular level, work is the transfer of energy that makes use of or drives the orderly motion of molecules in the surroundings. The uniform motion of the atoms in a piston driven back by expanding gas is an example of orderly molecular motion. In contrast, heat is the transfer of energy that makes use of or causes disorderly motion in the surroundings. When we say that a chemical reaction gives out heat, we mean that energy is leaving the reaction vessel and stimulating thermal motion (random molecular motion) in the surroundings.

The energy of a chemical system is stored in the potential and kinetic energies of the electrons and atomic nuclei. This stored energy is sometimes referred to as chemical energy; however, this is only a shorthand way of referring to the kinetic and potential energies of all the particles in an element or compound.

The internal energy of a system changes when a chemical reaction occurs because the electrons and nuclei settle into different arrangements, as in the change of partnerships of H and O atoms in the reaction $2\ H_2(g) + O_2(g) \rightarrow 2\ H_2O(g)$. The energy released in a chemical reaction can be transferred to the surroundings (and put to use) in a variety of ways regardless of the manner in which the energy accumulated in the first place. Thus, energy may escape as heat and be used to raise the temperature of the surroundings, including raising the temperature of water that is then employed in a turbine to do work. The energy may also escape as work. We have already discussed expansion work, using the example of a piston being driven. The work may be accomplished electrically, as when electrons are driven through an external circuit and used to drive an electric motor.

Atomic nuclei are also centers of energy storage as a result of their internal structures. This energy is released when the nucleons (protons and electrons) undergo rearrangement and thereby change the strength of their interactions. The changes in energy are so great that they give rise to measurable changes of mass. For all chemical processes, the changes in mass accompanying acquisition or loss of energy are totally negligible. SEE ALSO CHEMILUMINESCENCE; CHEMISTRY AND ENERGY; ELECTROCHEMISTRY; HEAT; PHYSICAL CHEMISTRY; SPECTROSCOPY; TEMPERATURE; THERMODYNAMICS.

Peter Atkins

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Energy Sources and Production

Modern societies rely on a variety of energy sources to heat homes, propel transportation vehicles, and produce goods for shelter, food, health care, and entertainment. Some of these sources are renewable, whereas others are nonrenewable. A renewable energy source, for example, solar energy, is one that is virtually inexhaustible on the human time scale. A nonrenewable energy source, for example, natural gas, is one that can be either completely consumed (during a lifetime, or during several lifetimes) or depleted to such an extent that it is no longer economical for humankind to obtain it. Figure 1 shows energy consumption in both the world and in the United States in 2001 by source.

Fossil Fuels

About 80 percent of commercial energy is obtained from three kinds of fuel: oil, coal, and natural gas. These fuels burn in air with the release of energy. They are called fossil fuels because they are believed to have formed from the remains of plants and animals subject to heat and pressure for millions of years.

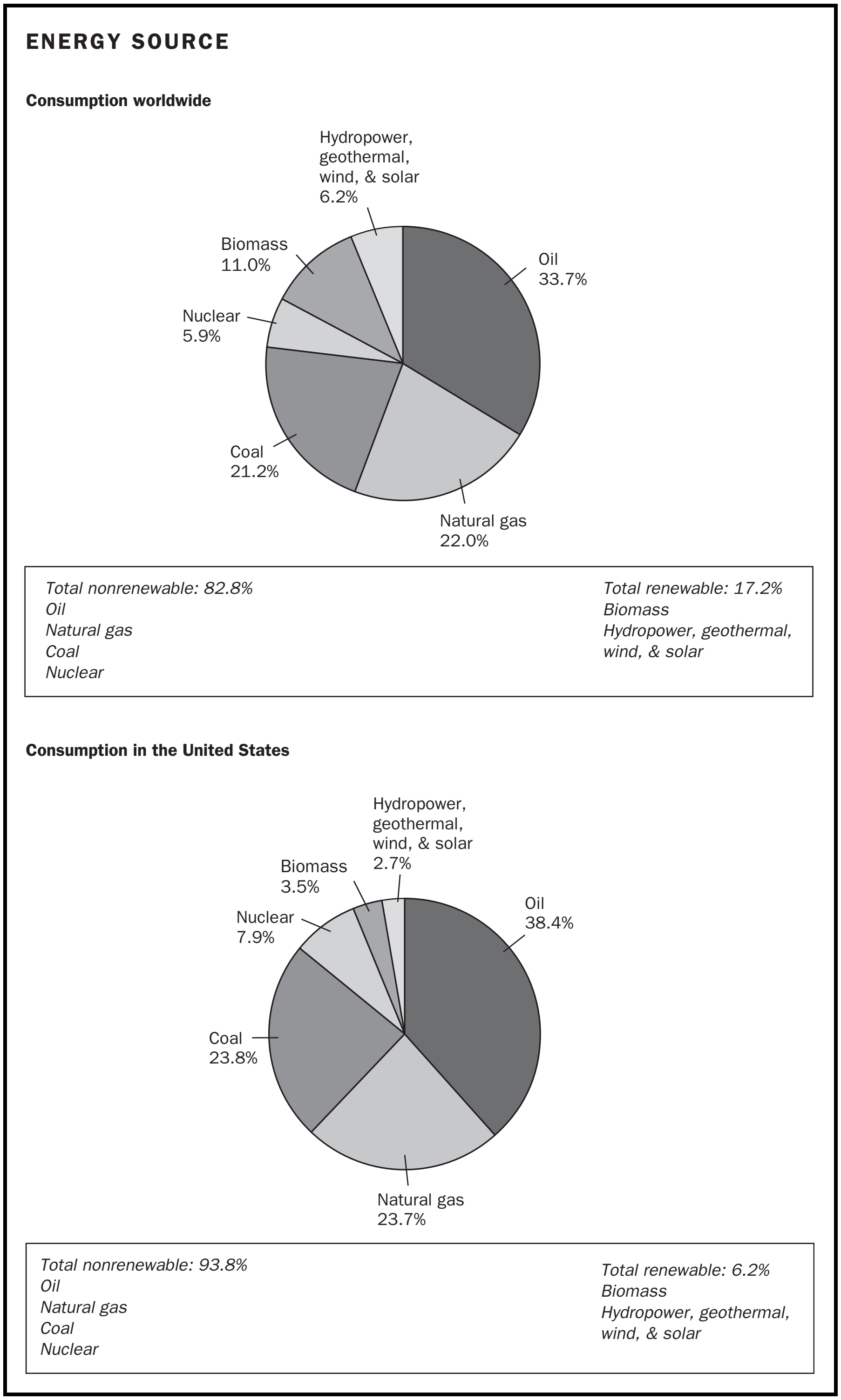

Figure 1. Sources of energy consumed worldwide and in the United States in 2001. In that year, the United States consumed a total of 1.0 x 10^{19} J of energy, whereas worldwide consumption was 4.2 x 10^{19} J. (Data was obtained from British Petroleum and the World Energy Council.)

Natural gas is a mixture of methane (CH_4), 60 to 90 percent, and smaller amounts of other gaseous hydrocarbons, including ethane (C_2H_6), propane (C_3H_8), and butane (C_4H_{10}). It is valued because it burns hotter and produces less air pollution than other fossil fuels. Complete **combustion** of a hydrocarbon substance produces carbon dioxide and water.

combustion: burning, the reaction with oxygen

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g) \qquad \Delta H = 50.1 \text{ kJ/g}$$

In 2001, 2.39 trillion cubic meters of natural gas were consumed worldwide, with estimated remaining reserves of 150 trillion cubic meters.

Oil (also referred to as petroleum) is a complex liquid mixture of organic substances, principally of hydrocarbons containing five to sixteen carbon atoms. Most crude oil, once removed from a well, is sent by pipeline to a refinery, where it is distilled to separate it into gasoline, heating oil, diesel oil, and asphalt. The use of catalysts during the refining process increases the yield of gasoline. In 2001, 25.7 billion barrels of oil were used worldwide, with estimated reserves of 1.05 trillion barrels. (One barrel contains 159 liters.)

Coal is the most plentiful fossil fuel, comprising 80 percent of the fuel reserves of the United States and 90 percent of those of the world. It is a complex mixture of organic compounds and is anywhere from 30 to 95 percent carbon by mass. It also contains sulfur compounds. When coal is burned, the sulfur is converted to sulfur dioxide, a troublesome air pollutant. The description of coal as being of high quality is based on its having a low sulfur content and a high carbon content. Lignite coal (brown coal) has a low carbon content and produces the least energy upon combustion (about 15 kJ/g). Bituminous coal (soft coal) has a higher carbon content and produces more energy. It is the most extensively used coal. Anthracite coal (hard coal) has the highest carbon and heat content (about 30 kJ/g), but supplies of it are limited in most places. In 2001, 4.41 billion metric tons of coal were consumed worldwide, with estimated reserves of 985 billion metric tons. (A metric ton is 1,000 kilograms [2,679 pounds].)

The combustion of fossil fuels produces carbon dioxide gas, a heat-trapping gas. For the past 250 years (since the beginning of the **Industrial Revolution**), the increased use of fossil fuels has caused the atmospheric concentration of carbon dioxide to increase by a factor of about 25 percent. It is now generally believed that this increase has produced higher global temperatures—a phenomenon called the **greenhouse effect**.

Industrial Revolution: widespread replacement of hand tools by power-driven machines, beginning about 1750 (especially in England)

greenhouse effect: presence of carbon dioxide in the atmosphere prevents heat from escaping, thereby raising Earth's temperature

fission: process of splitting an atom into smaller pieces

Nuclear Energy

Commercial nuclear power is generated by nuclear **fission** reactions. When slow-moving neutrons strike nuclei of uranium-235 or plutonium-239, these nuclei are split, releasing energy. The energy is used to heat water and drive a turbine, in turn producing electrical energy. Currently nuclear power supplies more than 16 percent of the world's total electricity.

A typical nuclear reactor utilizes uranium oxide, whose uranium content is approximately 3 percent uranium-235, and 97 percent uranium-238, by mass. During the fission reaction, the uranium-235 is consumed and fission products form. As the amount of uranium-235 decreases and the amounts of fission products increase, the fission process becomes less efficient. At some point, the spent nuclear fuel is removed and stored. Some of the radioactive fission products, because of their radioactivity and long half-lives, must be stored securely for thousands of years. Thus, nuclear waste management poses a tremendous challenge.

Scientists hope to someday use controlled nuclear fusion to produce energy. Nuclear fusion, which involves the coming together of light nuclei to form heavier ones, is the process by which stars generate energy. In order for nuclear fusion to occur, the nuclei must have extremely high temperatures. Research has focused on the fusion of deuterium (hydrogen-2) nuclei and tritium (hydrogen-3) nuclei, a process that requires about 50 million degrees Celsius.

Renewable Energy Sources

The principal renewable energy sources are **biomass** from crops such as trees and corn, hydropower from flowing rivers, geothermal power from heat stored in Earth, wind energy from the movement of winds, and solar energy from the Sun.

biomass: collection of living matter

Wood is part of an array of plant matter referred to as biomass that can be burned to produce energy. The combustible substances in biomass are primarily carbohydrates (and of these, primarily cellulose). Cellulose, whose simplest or empirical formula is CH_2O, undergoes combustion to form carbon dioxide and water.

$$CH_2O(s) + O_2(g) \rightarrow CO_2(g) + H_2O(g) \qquad \Delta H = -14 \text{ kJ/g}$$

Wood fuels continue to be used in the rural areas of developing countries.

Hydroelectric power is a well-developed energy source. Today, hydropower provides about 19 percent of the world's electricity supply. Because it is a clean, renewable source of energy, hydropower should continue to serve as a vital energy source.

There has been a rapid growth in the use of wind turbines to generate electricity. In 2001 the amount of electricity generated in this way worldwide corresponded to the amount that would have been obtained from burning 15 million barrels of oil. Although this represents only about 0.05 percent of worldwide energy production in 2001, this fraction will increase.

Solar energy is the most significant and promising renewable energy source. Solar energy is converted to electricity by solar cells (also known as photovoltaic cells). A great deal of solar energy is used currently in what is known as passive heating (which can be directly experienced as the heat gain in a greenhouse caused by sunlight). SEE ALSO AIR POLLUTION; CHEMISTRY AND ENERGY; COAL; ENERGY; FOSSIL FUELS; GLOBAL WARMING; NUCLEAR FISSION; NUCLEAR FUSION; PETROLEUM; SOLAR CELLS.

H. Eugene LeMay Jr.

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Environmental Pollution

Environmental pollution is the release of chemical waste that causes detrimental effects on the environment. Environmental pollution is often divided into pollution of water supplies, the atmosphere, and the soil. In his book *Environmental Chemistry*, Stanley Manahan lists several different types of pollutants, including toxic inorganic and organic compounds, high concentrations of normally innocuous compounds, and heat and noise. While much pollution is produced by the chemical industry, domestic sources include human waste and automobile exhaust.

While physical sources, such as noise and light, of pollution are important, people most often notice the damage of chemical pollution on animals and plant life. These chemicals can react with tissues in the body and change the structure and function of the organ, cause abnormal growth and development of the individual, or bind with the genetic material of cells and cause cancer. The study of the effects of poisons on the body is called **toxicology**. One of the central tenets of toxicology states that the dose of a chemical determines its overall effects and that most chemicals can be dangerous at high exposures.

toxicology: division of pharmacology dealing with poisons, their identification, detection, effects on the body, and remedies

Individuals and chemical and petroleum companies contribute to the pollution of the atmosphere by releasing inorganic and organic gases and particulates into the air. The atmosphere is a paper-thin layer of gas (representing 1 percent of the mass of Earth) that protects the planet from damaging cosmic and **ultraviolet radiation**, contains life-giving oxygen, and allows the efficient cooling of the planet.

ultraviolet radiation: portion of the electromagnetic spectrum with wavelengths shorter than visible but longer than x rays

Atmospheric Pollution

Some examples of atmospheric pollutants include nitrogen dioxide (NO_2), sulfur dioxide (SO_2), carbon monoxide (CO), and **chlorofluorocarbons (CFCs)**. The first two pollutants combine with water to form acids, which not only irritate the lungs but also contribute to the long-term destruction of the environment due to the generation of **acid rain**. Carbon monoxide, generated by the incomplete **combustion** of hydrocarbons, displaces and prevents oxygen from binding to hemoglobin and causes asphyxiation. Also, it binds with metallic pollutants and causes them to be more mobile in air and water. CFCs and other halogenated hydrocarbons react with light to form highly reactive species, called radicals, which destroy ozone in the upper atmosphere. These reactions greatly reduce the protective effects of ozone against ultraviolet radiation.

chlorofluorocarbon (CFC): compound that contains carbon, chlorine, and fluorine atoms, which removes ozone in the upper atmosphere

acid rain: precipitation that has a pH lower than 5.6; term coined by R. A. Smith during the 1870s

combustion: burning, the reaction with oxygen

Water Pollution

Fresh, clean, and drinkable water is a necessary but limited resource on the planet. Industrial, agricultural, and domestic wastes can contribute to the pollution of this valuable resource, and water pollutants can damage human and animal health. Three important classes of water pollutants are **heavy metals**, inorganic pollutants, and organic pollutants. Heavy metals include **transition metals** such as cadmium, mercury, and lead, all of which can contribute to brain damage. Inorganic pollutants like hydrochloric acid, sodium chloride, and sodium carbonate change the acidity, salinity, or alkalinity of the water, making it undrinkable or unsuitable for the support of animal and plant life. These effects can result in dire consequences for higher mammals such as humans. A list of organic pollutants includes pesticides such as chlorpyrifos and paraquat, and their byproducts, such as dioxin. All of these substances are highly lethal to animals, and many can be readily absorbed through the skin.

heavy metal: by convention, a metal with a density greater than 5 g/cm^3; 70 elements are thus classified as heavy metals

transition metals: elements with valence electrons in d-sublevels; frequently characterized as metals having the ability to form more than one cation

Pesticides

The use of pesticides in agriculture contributes to environmental pollution. Pesticides are used to control the growth of insects, weeds, and fungi, which compete with humans in the consumption of crops. This use not only increases crop yields and decreases grocery prices, but also controls diseases such as malaria and encephalitis. However, the spraying of crops and the water runoff from irrigation transports these harmful chemicals to the habitats of nontarget animals. Chemicals can build up in the tissues of these animals, and when humans consume the animals the increased potency of the pesticides is manifested as health problems and in some cases death. Chemists have recently developed naturally occurring pesticides that are toxic only to their particular targets and are benign to birds and mammals. The most significant pesticide of the twentieth century was DDT, which was highly effective as an insecticide but did not break down in the environment and led to the death of birds, fish, and some humans.

Industrial Pollution and Love Canal

The infamous case of the pollution of Love Canal, on Lake Erie in New York, brought environmental pollution to the public attention in the 1970s, and the history of this incident has been thoroughly described at a University of Buffalo web site. From 1942 to 1953, several chemical companies dumped 20,000 metric tons of chemical waste at this site. In 1953 the land was sold to the local board of education, and the 99th Street School was constructed on the land. The school attracted families to the neighborhood, which grew to contain 800 single-family homes and 240 apartment units by 1978. Unfortunately, eighty different chemicals, including dioxins and polychlorinated biphenyls (PCBs), started to leach through the soil, and residents began complaining of odd smells in their houses and experiencing many unexplainable health problems. The school was closed in August 1978,

ERIN BROCKOVICH: THE STORY BEHIND THE MOVIE

In December 1987, Pacific Gas and Electric (PG&E) reported to the Environmental Protection Agency that it had detected levels of chromium (VI) at its natural gas compression station near Hinkley, California, that were ten times higher than those allowed by government standards. These reports devalued land in the community and sparked the curiosity of Erin Brockovich, who was working in a law office as a secretary. Her passionate investigation into the actions of the large public utility led to the discovery of a thirty-year cover-up of the improper disposal of cooling water contaminated with the chromium(VI). Dr. Robert A. Goyer has stated that chromium (VI) irritates the skin of humans and causes cancer in laboratory animals. According to an article by attorney Carole Bos on the *LawBuzz* web site, Erin Brockovich's work forced PG&E to pay damages of $300 million to the residents of Hinkley.

and the federal government contributed $10 million for the relocation of 200 families nearest the site. In 1980 President Carter sent additional funds, for the relocation of 700 more families. Today federal laws stipulate that generators of hazardous waste are responsible for the proper storage and disposal chemicals from the "cradle to the grave."

New Pollutants: Toxic Mold

Recently many people have complained of illnesses associated with the presence of toxic mold in their homes and workplaces. These molds, which thrive in damp surroundings, are members of the fungi kingdom and produce chemicals called mycotoxins that can produce a variety of health problems. Additionally, molds produce strong allergic reactions in some individuals. According to the Centers for Disease Control and Prevention (CDC), little strong evidence exists that can tie all of the health problems seen in damp or flooded areas to molds, but the CDC also recommends that one should repair leaking plumbing and all other causes of damp environments as soon as they occur.

While some of the environmental pollution created in society is avoidable, industrial nations will always produce a low level of pollutants. Pesticides greatly increase overall food production; pharmaceuticals, which require organic chemicals for their manufacture, extend life; and plastics are used in all aspects of medical and domestic life. Society must find a balance between the desire to minimize the cost of manufactured items and the desire to require industries and individuals to reduce pollution. SEE ALSO AIR POLLUTION; WATER POLLUTION.

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Enzymes

Enzymes are (mostly) proteins that catalyze biochemical reactions; that is, they increase the rate of a reaction but are not used up in the process. Their importance to life is underscored by the fact that many severe or fatal genetic diseases involve a missing or defective enzyme. Enzymes can also provide targets, with hitting the target the strategy for attacking disease-causing bacteria or viruses. One could design a drug that attaches to or occupies the active site of a target organism's enzyme. For example, penicillin destroys an enzyme crucial to the **synthesis** of bacterial cell walls. In the treatment of AIDS, HIV protease inhibitors target the viral enzyme protease.

synthesis: combination of starting materials to form a desired product

Properties and Mechanism

In some cases, the increase in the rate of an enzyme-catalyzed reaction versus the uncatalyzed rate is a millionfold. As soon as one reaction has been catalyzed, the enzyme is available for another round of **catalysis**—a phenomenon known as turnover. Enzymes operate near physiological temperature and pH, and they are also highly specific in their actions—for example, an enzyme called hexokinase will place a phosphate group only onto the sixth carbon of a D-glucose molecule. The enzyme has no activity toward L-glucose, and reduced activity toward other D-sugars. Enzymes can also be regulated so that they are switched on only when they are needed by the cell. They may consist of a single **polypeptide** chain of amino acids (RNAse contains 124 amino acids), or they may require an additional chemical called a coenzyme. Many of the **vitamins** as well as several **metals** act as coenzymes.

catalysis: the action of effect of a substance in increasing the rate of a reaction without itself being converted

polypeptide: compound containing two or more amide units—C(O)NH—produced by the condensation of two or more amino acids

vitamins: organic molecules needed in small amounts for the normal function of the body; often used as part of an enzyme catalyzed reaction

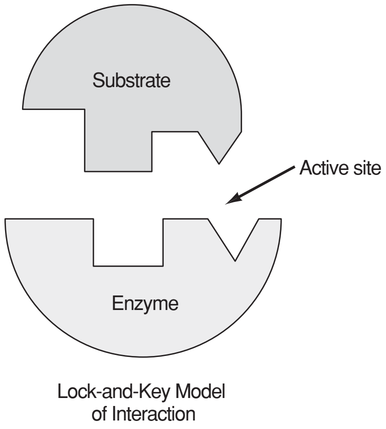
metal: element or other substance the solid phase of which is characterized by high thermal and electrical conductivities

A study of enzyme catalysis is a study of kinetics, which asks the question "how fast?" However, enzymes cannot alter the outcome or direction of a reaction. For instance, if one were to add a small amount of sodium chloride to a large volume of water, we know that the end result will be that the salt will dissolve in the water. However, the time dissolution takes depends on a number of factors: What is the temperature?; Is it being stirred? This is kinetics. We also know that a swinging pendulum will eventually come to rest at its **equilibrium** point, which in this case is its pointing straight down toward the center of Earth. Kinetics describes only the time it takes to reach that point. Enzymes cannot alter the equilibrium point of a reaction, only the time it takes to get there.

equilibrium: condition in which two opposite reactions are occurring at the same speed, so that concentrations of products and reactants do not change

To proceed to products, reactants must come together with sufficient energy to overcome an energy barrier known as the energy of activation. The apex of this barrier represents the transition state between reactants and products. Enzymes act to lower the energy of activation by stabilizing (lowering the energy of) the transition state.

Mechanistically, an enzyme will bind the reactant, called the substrate, at a very specific site on the enzyme known as the active site. This resulting enzyme–substrate complex (ES), described as a lock-and-key mechanism, involves weak binding and often some structural changes—known as induced fit—that assist in stabilizing the transition state. In the unique microenvironment of the active site, substrate can rapidly be converted to product resulting in an enzyme=product (EP) complex that then dissociates to release product.



A lock-and-key model of the interaction of an enzyme and substrate.

Nomenclature

Enzyme nomenclature has historically been at the whim of the discoverer of the enzyme. Many enzyme names give clues to their actions or to where they are found. The meat tenderizer papain can be obtained from the papyrus plant. Pepsin is a digestive enzyme found in the stomach. Lysozyme acts to lyse bacterial cell walls. Most enzymes are now named by their function along with the suffix "–ase." For instance, ethanol is metabolized in the liver by alcohol dehyrogenase. Phosphates are removed from molecules by phosphatases. An international body known as the Enzyme Commission (EC) has assigned numerical designations, called EC numbers, to enzymes. The EC has listed six categories based on type of activity (oxidation-reduction, hydrolysis, etc.), along with several subcategories, into which enzymes are placed. For example, alcohol dehydrogenase is EC 1.1.1.1.

Enzyme Kinetics

The rate of an enzyme-catalyzed reaction varies with the substrate concentration. At very low substrate concentrations, the rate will be directly proportional to the concentration of the substrate and will exhibit first-order kinetics. However, at very high substrate levels, all of the active sites are occupied and substrate molecules must wait their turn, just as the traffic at a line of tollbooths depends on how fast the cars can pass through the gates. This represents saturation, and the reaction rate is at its maximum and is designated V_{max}.

Other factors that influence enzyme activity include pH and temperature. Most mammalian enzymes operate maximally at around physiological pH and body temperature. There are several exceptions. The stomach digestive enzyme pepsin works best at around pH 2.0, the approximate pH of the stomach. Bacteria found in hot springs have enzymes that operate at or near the boiling point of water. In most cases, however, extremes of pH or temperature will destroy enzymes in an enzyme-unfolding process known as denaturation. Only one, very precise, three-dimensional configuration or fold of the chain of amino acids is functional. Denatured or unfolded proteins are inactive. Denaturation can be observed when an egg white is cooked: The proteins in the egg white unfold and form a gel-like aggregate with other unfolded proteins. The same occurs when bacteria spoil milk by lowering its pH sufficiently to unfold and curdle milk proteins.

RNA as an Enzyme

Although enzymes are considered to be proteins, enzyme activity has recently been found in ribonucleic acid (RNA) in certain organisms. These "ribozymes" may yield clues to the origins of life on Earth. **DNA** needs

DNA: deoxyribonucleic acid—the natural polymer that stores genetic information in the nucleus of a cell

enzymes to replicate, whereas enzymes need the instructions of DNA. This represents a "chicken-and-egg" question that has stumped researchers. Early life may have used RNA that was able to catalyze its own replication. SEE ALSO Catalysis and Catalysts; Coenzyme; Denaturation; Hydrogen; Inhibitors; Kinetics; Proteins; Ribonucleic Acid.

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Epinephrine

Epinephrine, also known as **adrenalin**, is a hormone that is responsible for the "fight or flight" reaction in mammals. Chemically, it mobilizes the body's defense system, inducing the release into the blood of large amounts of **glucose** from stores in the liver and muscles. This burst of energy is the familiar "adrenalin rush" one experiences when frightened or excited. In some tissues, epinephrine also acts as a neurotransmitter, conveying signals between adjacent nerve cells.

adrenalin: chemical secreted in the body in response to stress

glucose: common hexose monosaccharide; monomer of starch and cellulose; also called grape sugar, blood sugar, or dextrose

Epinephrine (see Figure 1) is synthesized in several steps from either phenylalanine or **tyrosine** (both amino acids). Two adjacent hydroxyl groups are placed on the aromatic ring, leading to the ring structure called catechol. These hydroxylations form the **intermediate** L-dopa, which in turn is converted to dopamine (a neurotransmitter), norepinephrine (also a neurotransmitter), and finally epinephrine. Epinephrine together with norepinephrine and dopamine make up the family of biogenic amines called catecholamines.

tyrosine: one of the common amino acids

intermediate: molecule, often short-lived, that occurs while a chemical reaction progresses but is not present when the reaction is complete

Nerve signals to the adrenal gland activate the conversion of stores of norepinephrine to epinephrine and its release into the bloodstream. The fight or flight reaction includes increased blood glucose, increased vasoconstriction in certain parts of the body, and increased heart rate. At the cellular level, epinephrine binds to liver and muscle cells at specific **receptors** on the outside surface of cell membranes. Such a receptor then activates a series of enzymatic reactions inside the cell, culminating in the **synthesis** of large amounts of cyclic adenosine monophosphate (cAMP). Epinephrine cannot cross the cell membrane, so its hormonal signal is transmitted inside the cell via cAMP, acting as a second messenger (epinephrine being the first messenger). CyclicAMP switches on a cascade of enzymes—mostly kinases that place a phosphate group at specific sites on other proteins or enzymes. These phosphorylations serve to activate (or in some cases inhibit) enzymatic reactions. The end result is the activation of glycogen phosphorylase, an enzyme that breaks down glycogen into its glucose units, and the release of glucose into the bloodstream.

receptor: area on or near a cell wall that accepts another molecule to allow a change in the cell

synthesis: combination of starting materials to form a desired product

The neurotransmitter action of epinephrine is terminated by reuptake into the neuron that released it, or breakdown to inactive **metabolites** by the enzymes catechol-O-methyl transferase (COMT) and monoamine oxidase (MAO). The second messenger effects inside the cell are terminated by enzymes that break down cAMP, and by phosphatases that reverse the action of the kinases by removing phosphates.

metabolites: products of biological activity that are important in metabolism

Epinephrine also acts at a crucial regulatory step in the synthesis of fatty acids. The activity of the first enzyme in fatty acid synthesis, acetyl-coenzyme A (AcCoA) carboxylase, is regulated by **phosphorylation**. The phosphorylated enzyme is inactive (and subsequent fatty acid synthesis is halted), whereas the dephosphorylated enzyme is active. Epinephrine, through the second messenger cAMP, prevents the dephosphorylation of AcCoA carboxylase, rendering it inactive and halting the synthesis of fatty acids. Indeed, during the fight or flight reaction, the organism needs to release energy in the form of glucose and fatty acids rather than store energy as glycogen or fat.

Clinically, epinephrine plays a lifesaving role in countering the effects of anaphylactic shock. Histamines released in large amounts upon the body's exposure to an allergen (bee stings in certain individuals, for instance) can constrict smooth muscle, including that in the airway passages. Epinephrine does the opposite: It relaxes smooth muscle, though at different receptors. Its effects on heart muscle (increasing the heart rate) can be used as a lifesaving measure when a patient's heart has stopped. Epinephrine is also used in conjunction with local anesthetics such as lidocaine. By constricting blood vessels near the site of the injection, it keeps the anesthetic from diffusing away from the site. SEE ALSO Kinase.

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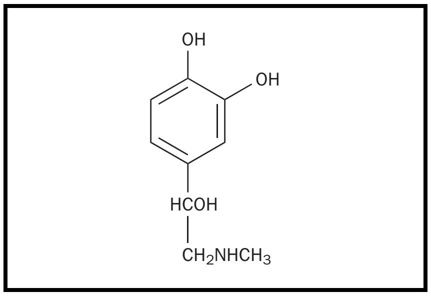

Figure 1. Chemical structure of epinephrine.

phosphorylation: the process of addition of phosphates into biological molecules

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Equations, Chemical

Chemical reactions convert reactants to products, whose properties differ from those of the reactants. Chemical equations are a compact and convenient way to represent chemical reactions. They have the general form

$$\text{Reactant(s)} \rightarrow \text{Product(s)}$$

The arrow in the equation means "changes to" or "forms." The reaction of gaseous nitrogen with hydrogen to produce ammonia, NH_3, is represented by the chemical equation

$$\underbrace{N_2 + 3\ H_2}_{\text{Reactants}} \rightarrow \underbrace{2\ NH_3}_{\text{Product}}$$

Although there are thousands of chemical reactions, a significant number of them, especially those that are not organic reactions, can be classified according to four general patterns: combination, decomposition, displacement, and exchange.

1. Combination. A combination reaction is one in which two or more substances (the reactants) are combined directly to form a single product (the product). An example is the reaction in which sodium (Na) combines with chlorine (Cl_2) to form sodium chloride, or table salt (NaCl).

A reaction of sodium with chlorine to produce sodium chloride is an example of a combination reaction.

$$2\ \mathrm{Na} + \mathrm{Cl_2} \rightarrow 2\ \mathrm{NaCl}$$

The physical states of reactants and products are included where necessary. The symbols used are: (*s*) for solid, (*l*) for liquid, (*g*) for gas, and (*aq*) for aqueous (water) solutions. In the case of sodium chloride formation, the equation is modified accordingly.

$$2\ \mathrm{Na}\ (s) + \mathrm{Cl_2}\ (g) \rightarrow 2\ \mathrm{NaCl}\ (s)$$

2. Decomposition. A decomposition reaction can be considered to be the reverse of a combination reaction. In a decomposition reaction, one substance (the reactant) decomposes to form two or more products. For example, calcium carbonate (limestone) decomposes at high temperatures to calcium oxide (lime) and carbon dioxide. This reaction is used industrially to produce large quantities of lime.

$$\underset{\substack{\text{calcium}\\\text{carbonate}}}{\mathrm{CaCO_3}}\ (s) \rightarrow \underset{\substack{\text{calcium}\\\text{oxide}}}{\mathrm{CaO}}\ (s) + \mathrm{CO_2}\ (g)$$

3. Displacement. A displacement reaction (also called a single replacement reaction) occurs when an element reacts with a compound to form a new compound and release a different element. An example is the reaction that releases silicon (Si) from silicon dioxide (sand), SiO_2, via its reaction with carbon. Carbon monoxide, CO, is the reaction's other product. When further purified, the silicon can be used in computer chips.

$$\mathrm{SiO_2}\ (s) + 2\ \mathrm{C}\ (s) \rightarrow \mathrm{Si}\ (s) + 2\ \mathrm{CO}\ (g)$$

4. Exchange. During an exchange reaction, "partners" in compounds exchange their partners. One type of exchange reaction is called a neutralization reaction, the reaction between an acid and a base. The reaction of sodium hydroxide (lye), NaOH, with hydrochloric acid, HCl, to produce NaCl and water is such a reaction. In this case, Na^+ switches partners from OH^- to Cl^-, and H^+ from $Cl^-$to OH^-.

$$\mathrm{NaOH}\ (aq) + \mathrm{HCl}\ (aq) \rightarrow \mathrm{NaCl}\ (aq) + \mathrm{H_2O}\ (l)$$

Organic chemical reactions, those in which carbon plays a predominant role, are very important in biochemical systems and industrial processes. These reactions can also be represented by balanced chemical equations, a few examples of which are given.

The fermentation of glucose to produce ethyl alcohol (ethanol)

$$\underset{\text{glucose}}{\mathrm{C_6H_{12}O_6}} \rightarrow 2\ \underset{\text{ethanol}}{\mathrm{C_2H_5OH}} + 2\ \mathrm{CO_2}$$

The synthesis of acetylsalicylic acid (aspirin) from the reaction of salicylic acid with acetic anhydride

$$2\ \underset{\substack{\text{salicylic}\\\text{acid}}}{\mathrm{C_7H_6O_3}} + \underset{\substack{\text{acetic}\\\text{anhydride}}}{\mathrm{C_4H_6O_3}} \rightarrow 2\ \underset{\text{aspirin}}{\mathrm{C_9H_8O_4}} + \mathrm{H_2O}$$

The formation of a triglyceride (a fat), such as the biochemical synthesis of tristearin via the reaction of stearic acid with glycerol:

$$3\ \underset{\substack{\text{stearic}\\\text{acid}}}{\mathrm{C_{18}H_{36}O_2}} + \underset{\text{glycerol}}{\mathrm{C_3H_8O_3}} \rightarrow \underset{\text{tristearin}}{\mathrm{C_{57}H_{110}O_6}} + 3\ \mathrm{H_2O}$$

Matter is conserved in chemical reactions: *The total mass of the products equals the total mass of the reactants.* Chemical equations reflect this conservation. It is why chemical equations must be balanced. Atoms have mass, and the numbers of each kind of atom on each side of the equation must be the same. Coefficients, the numbers to the left of the formulas, are used to balance equations. Many equations can be balanced directly by simply adjusting the coefficients, as illustrated in the equations given above. Other equations are more difficult to balance, such as that for the decomposition of nitroglycerine (an explosive)

$$4\ C_3H_5(NO_3)_3\ (l) \rightarrow 12\ CO_2\ (g) + 10\ H_2O\ (l) + 6\ N_2\ (g) + O_2\ (g)$$

and this complicated reaction involving several reactants and products

$$4\ CuSCN + 7\ KIO_3 + 14\ HCl \rightarrow 4\ CuSO_4 + 7\ KCl + 4\ HCN + 7\ ICl + 5\ H_2O$$

Balanced chemical equations provide a significant amount of information. Consider the equation for photosynthesis, the natural process by which green plants form glucose, $C_6H_{12}O_6$, and oxygen from the reaction of carbon dioxide with water.

$$\underbrace{6\ CO_2 + 6\ H_2O}_{\text{Reactants}} \rightarrow \underbrace{C_6H_{12}O_6 + 6\ O_2}_{\text{Products}}$$

This balanced equation and its coefficients can be interpreted as indicating that six carbon dioxide molecules and six water molecules react to form one molecule of glucose and six oxygen molecules, each containing two oxygen atoms. A coefficient multiplies the term following it. The "6 CO_2" denotes six CO_2 molecules containing a total of six carbon atoms and twelve oxygen atoms.

$$6\ CO_2 \text{ molecules} \times \frac{1\text{C atom}}{1CO_2 \text{ molecule}} = 6 \text{ C atoms}$$

$$6\ CO_2 \text{ molecules} \times \frac{2 \text{ O atoms}}{1CO_2 \text{ molecule}} = 12 \text{ O atoms}$$

Applying these concepts to the remainder of the balanced equation yields information that confirms that the equation is balanced—the atom counts for both sides of the equation are the same.

Reactants	Products
Carbon atoms = 6	Carbon atoms = 6
Hydrogen atoms = 12	Hydrogen atoms = 12
Oxygen atoms = 12 + 6 = 18	Oxygen atoms = 6 + 12 = 18

Coefficients also apply to a larger scale, in which the counting unit is the mole (there are 6.02×10^{23} molecules per mole of a compound), rather than individual molecules. Thus, this balanced equation also represents the reaction of six moles of glucose with six moles of water to produce one mole of glucose and six moles of oxygen.

Oxidation-reduction (redox) reactions are an important, general kind of reaction, one involving the transfer of electrons. Oxidation is the *loss* of an electron or electrons from an element, ion, or compound. Reduction is the *gain* of an electron or electrons from an element, ion, or compound. The two processes occur simultaneously; electrons released during oxidation are gained in a reduction process. In every redox reaction, a reactant is oxidized (loses electrons) and a reactant is reduced (gains electrons). During a redox reaction there is a change in oxidation numbers—evidence of a redox reaction. An oxidation number compares the charge of an uncombined atom, one not in a compound, with its actual or relative charge when it is part of a compound. Oxidation numbers are zero, positive, or negative.

These guidelines are used to determine oxidation numbers.

- Atoms of pure elements, that is, atoms not combined with any *other* element, have an oxidation number of zero. For example, sodium in metallic sodium, Na; oxygen in molecular oxygen, O_2; and chlorine in molecular chlorine, Cl_2, each have an oxidation number of 0.
- Monatomic ions have an oxidation number equal to the charge of the ion. Thus, a sodium ion, Na^+, has an oxidation number of +1; that of chlorine in a chloride ion, Cl^-, is −1.
- Generally, hydrogen atoms in compounds have an oxidation number of +1; oxygen atoms in compounds are typically −2.
- The sum of oxidation numbers in a neutral compound is zero. Water, H_2O, is an example. Hydrogen: $2\ H \times (+1/H) = +2$; oxygen: $1\ O \times (-2/O) = -2$; $(+2) + (-2) = 0$
- The sum of oxidation numbers of the atoms in a polyatomic ion equals the charge on the ion. For example, the sulfate ion, SO_4^{-2}, a polyatomic ion, has a net charge of −2. Each oxygen in a sulfate ion has an oxidation number of −2, and four oxygens add up to −8. For the sulfate ion to have a net −2 charge, sulfur must have a +6 oxidation number: $-2 = 4(-2) + 6$.

Oxidation numbers and their changes can be used to identify the reaction of sodium with chlorine to form NaCl as a redox reaction.

$$2\ Na + Cl_2 \rightarrow 2\ NaCl$$

Reactant	Products
Oxidation number	Oxidation number
$Na = 0$	$Na^+ = +1$
$Cl = 0$	$Cl^- = -1$

During this reaction, reactant sodium atoms (oxidation number 0) are converted to sodium ions (oxidation number +1); reactant chlorine atoms (oxidation number 0) are transformed to chloride ions (oxidation number −1). Because there is a change in the oxidation numbers of the reactants during the reaction, this is a redox reaction. The definitions of oxidation and reduction can be broadened a bit using oxidation numbers: Oxidation is an *increase* in oxidation number; reduction is a *decrease* in oxidation number. The gain in oxidation number occurs because electrons are lost during oxidation; the gain of electrons during reduction causes a decrease in the oxidation number. This can be shown by using so-called half-reactions for each process.

$$\text{Oxidation half-reaction: } Na \rightarrow Na^+ + e^-$$

$$\text{Reduction half-reaction: } Cl_2 + 2\ e^- \rightarrow 2\ Cl^-$$

Notice in the balanced equation that two moles of Na were used to react with the two moles of chlorine atoms in one mole of Cl_2. Each mole of Na lost one mole of electrons; each mole of chlorine atoms gained a mole of electrons. Two moles of electrons were transferred to form two moles of NaCl. The overall reaction is the sum of the two half-reactions; the moles of electrons cancel, and the sodium ions and chloride ions combine to form sodium chloride. Note that the sum of the oxidation numbers in sodium chloride is zero: $(+1) + (-1) = 0$.

$$\text{Oxidation half-reaction: } 2\ \mathrm{Na} \rightarrow 2\ \mathrm{Na}^{+} + 2\ e^{-}$$

$$\text{Reduction half-reaction: } \mathrm{Cl}_2 + 2\ e^{-} \rightarrow 2\ \mathrm{Cl}^{-}$$

$$\text{Overall reaction: } 2\ \mathrm{Na} + \mathrm{Cl}_2 \rightarrow 2\ \mathrm{NaCl}$$

Oxidation-reduction reactions, even complex ones, can be balanced using either the half-reaction method or the oxidation number method. The half-reaction method will be discussed first, using the reaction of iron with chlorine to produce iron chloride.

$$\mathrm{Fe} + \mathrm{Cl}_2 \rightarrow \mathrm{FeCl}_3 \text{ (unbalanced equation)}$$

Half-Reaction Method

Step 1. Divide the reaction into two half-reactions; one corresponding to oxidation, the other, reduction.

$$\text{Oxidation: } \mathrm{Fe} \rightarrow \mathrm{Fe}^{3+}$$

$$\text{Reduction: } \mathrm{Cl}_2 + \rightarrow \mathrm{Cl}^{-}$$

Step 2. Balance each half-reaction for mass and then charge. The iron half-reaction is balanced with respect to mass because there is one iron on each side. However, the charge is not balanced; the left side has a charge of zero, the right side has a charge of +3. Charge is balanced by adding three electrons to the right side.

$$\mathrm{Fe} \rightarrow \mathrm{Fe}^{3+} + 3\ e^{-}$$

The chlorine half-reaction is unbalanced in terms of mass and charge. Mass balance is achieved by using a coefficient of 2 on the right side.

$$\mathrm{Cl}_2 \rightarrow 2\ \mathrm{Cl}^{-}$$

Charge is then balanced by adding two electrons to the left side.

$$\mathrm{Cl}_2 + 2\ e^{-} \rightarrow 2\ \mathrm{Cl}^{-}$$

The two half-reactions indicate that three electrons are lost per Fe atom during oxidation, and that two electrons are gained as each Cl_2 molecule is reduced.

Step 3. Combine the two half-reactions in such a way as to balance the electrons lost and gained. The oxidation half-reaction lost three electrons; the reduction half-reaction gained two electrons. Therefore, to balance electrons lost and gained, multiply the oxidation half-reaction by 2 and the reduction half-reaction by 3. Add the resulting half-reactions to get the final balanced equation for the formation of $FeCl_3$. Note that, in doing so, the electrons cancel (as they should if the final equation is balanced).

$$2\ [\mathrm{Fe} \rightarrow \mathrm{Fe}^{3+} + 3\ \mathrm{e}^{-}] \rightarrow 2\ \mathrm{Fe} \rightarrow 2\ \mathrm{Fe}^{3+} + 6\ e^{-}$$

$$3\ [Cl_2 + 2\ e^- \rightarrow 2\ Cl^-] \rightarrow 3\ Cl_2 + 6\ e^- \rightarrow 6Cl^-$$

The Fe^{3+} and Cl^- ions combine to form $FeCl_3$ and the overall balanced equation is

$$2\ Fe + 3\ Cl_2 \rightarrow 2\ FeCl_3$$

The half-reaction method can be applied to more complex redox reactions, such as the reaction of permanganate ion, MnO_4^-, with Fe^{2+} in acidic solution.

$$MnO_4^-\ (aq) + Fe^{2+}\ (aq) \rightarrow Mn^{2+}\ (aq) + Fe^{3+}\ (aq)\ \text{(unbalanced equation)}$$

Step 1. Oxidation: $Fe^{2+}\ (aq) \rightarrow Fe^{3+}\ (aq)$
Reduction: $MnO_4^-\ (aq) \rightarrow Mn^{2+}\ (aq)$

Step 2. Mass and charge balance are achieved this way:

The iron is balanced by adding one electron on the right

$$Fe^{2+}(aq) \rightarrow Fe^{3+}\ (aq) + e^-$$

To balance oxygen, we use H_2O on the right side; to balance hydrogen, we use H^+ on the left side (recall that the reaction is taking place in acidic solution)

$$8\ H^+\ (aq) + MnO_4^-\ (aq) \rightarrow Mn^{2+}\ (aq) + 4\ H_2O\ (l)$$

The reduction half-reaction has a net charge of +7 on the left [(8+) + (−1)] and +2 on the right [(+2) + 0]. Adding 5 electrons to the left side balances the charge.

$$8\ H^+\ (aq) + MnO_4^-\ (aq) + 5\ e^- \rightarrow Mn^{2+}\ (aq) + 4\ H_2O\ (l)$$

Step 3. Equalize the electrons transferred. Multiply the oxidation half-reaction by 5. Add the half-reactions, canceling the electrons.

$$5\ Fe^{2+}\ (aq) \rightarrow 5\ Fe^{3+}\ (aq) + 5\ e^-$$

$$8\ H^+\ (aq) + MnO_4^-\ (aq) + 5\ e^- \rightarrow Mn^{2+}\ (aq) + 4\ H_2O(l)$$

Balanced equation: $5\ Fe^{2+}\ (aq) + 8\ H^+\ (aq) + MnO_4^-\ (aq) \rightarrow$
$5\ Fe^{3+}\ (aq) + Mn^{2+}\ (aq) + 4\ H_2O\ (l)$

Oxidation Number Method

$MnO_4^-\ (aq) + Fe^{2+}(aq) + H^+\ (aq) \rightarrow$
$Mn^{2+}\ (aq) + Fe^{3+}\ (aq)\ H_2O\ (l)$ (unbalanced equation)

As in the half-reaction method, H_2O is used to balance oxygen, and H^+ is used to balance hydrogen.

Step 1. Identify the oxidation number of each element on each side of the equation. Determine which has undergone oxidation and which has undergone reduction. This is indicated in Table 1.

Element	Oxidation Number as Reactant	Oxidation Number as Product	Change in Oxidation Number	Oxidation or Reduction
Mn	+7	+2	Decrease by 5	Reduction
O	−2	−2	0	Neither
Fe	+2	+3	Increase by 1	Oxidation
H	+1	+1	0	Neither

Table 1.

Step 2. Use coefficients so that the total increase in oxidation number equals the total decrease. In this case, the total decrease is 5 (Mn^{+7} becomes Mn^{2+}), and the total increase must also be 5; each iron must be multiplied by 5: (5 Fe^{2+} becomes 5 Fe^{3+}). Balance hydrogen and oxygen in the usual manner. The balanced equation is

$$MnO_4^- (aq) + 5\, Fe^{2+} (aq) + 8\, H^+ (aq) \rightarrow Mn^{2+} (aq) + 5\, Fe^{3+} (aq) + 4\, H_2O (l)$$

SEE ALSO Chemical Reactions; Inorganic Chemistry; Mole Concept; Organic Chemistry.

Conrad L. Stanitski

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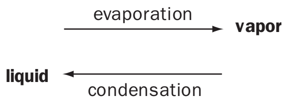
Equilibrium

A state of equilibrium exists in a process when the rate of the forward process equals the rate of the reverse process. The equilibrium condition exists in relation to thermal, mechanical, and chemical changes. For example, within a closed flask, liquid water evaporates to form vapor, and at the same time the vapor condenses to form liquid. When the rate of evaporation equals the rate of condensation, the system is said to be in a state of equilibrium:



A state of thermal equilibrium exists when the heat loss of a system is equal to the heat gain. Chemical equilibrium exists when a reversible chemical reaction occurs within a closed system, such as a sealed flask, and the rate of the reaction in the forward direction equals the rate of the reaction in the reverse direction. For example: $N_2 + 3H_2 \rightleftarrows 2NH_3$.

In this reaction, nitrogen and hydrogen gases react to form gaseous ammonia, NH_3. When nitrogen and hydrogen are first introduced into the reaction chamber, they begin to form ammonia molecules. As the concentration of ammonia increases, ammonia molecules start to decompose, forming nitrogen and hydrogen. When the rate at which ammonia is formed equals the rate at which it decomposes, the system is at equilibrium. A reaction at equilibrium never goes completely to completion; molecules of reactants continue to collide to form product molecules, and product molecules constantly decompose to form reactant molecules.

A state of mechanical equilibrium is a special physical state in which the external forces and moments on an object are zero. All forces are balanced, and the object is at rest. Examples of systems in mechanical equilibrium include a ball hanging motionless on a string and a mass suspended motionless from a spring.

Every equilibrium system follows predictable mathematical rules. The law of mass action states that the product of the concentrations of a reaction's products, each raised to the power of the coefficient of the species, divided by the product of the concentrations of the reactants, each raised to the power of the coefficient of the species, is a constant at constant temperature. Thus for the ammonia reaction:

$$N_2 + 3\ H_2 \rightleftarrows 2\ NH_3$$

The equation describing the equilibrium reaction is called an equilibrium expression, and K_{eq}, the equilibrium constant, is a definite numerical value for each equilibrium reaction. The equilibrium constant for a particular reaction is specific for that reaction and changes only with variations in temperature. The presence of a catalyst does not alter K_{eq} but does cause the reaction to reach equilibrium more rapidly.

The size of K_{eq} can be used to predict whether the reaction goes further toward completion (results in the formation of large quantities of products) or favors reactants (results in higher concentrations of reactants present at equilibrium). For example, hydrogen and iodine react at 200°C (392°F) to form hydrogen iodide in the following equilibrium reaction: $H_2 + I_2 \rightleftarrows 2HI$. The value of K_{eq} for the reaction has been determined to be 50, experimentally. At equilibrium, if the concentrations of hydrogen and iodine were 1.0 moles per liter, the concentration of hydrogen iodide would be $\sqrt{50}$ or 7.1 moles per liter.

$$K_{eq} = \frac{[NH_3]^2}{[N_2]\ [H_2]^3}$$

Le Châtelier's principle states that if a stress is brought to bear upon a system at equilibrium, the equilibrium reaction shifts in a direction that relieves the stress. Put more simply, if the concentration of one of the reactants or products is increased at equilibrium, the reaction moves in the direction that consumes the added material. Adding hydrogen and iodine to the reaction mixture above would result in the formation of more hydrogen iodide.

STP: standard temperature and pressure

Similarly, adding hydrogen and nitrogen to the reaction mixture that forms ammonia would result in the formation of more ammonia, and removing ammonia would shift the equilibrium to the right, forming even more ammonia. Ammonia, hydrogen, and nitrogen are all gases, and one mole of each gas occupies a volume of about 22.4 liters at **STP**. In the reaction $N_2 + 3H_2 \rightleftarrows 2NH_3$, 22.4 liters of nitrogen react with 3 times 22.4 liters of hydrogen to form 44.8 liters of ammonia. This means that 4 times

22.4 liters of reactants form 2 times 22.4 liters of products. Le Châtelier's principle predicts that increasing pressure on the system at equilibrium causes the equilibrium to shift to the right. Therefore, ammonia is manufactured in a continuous loop by pumping in N_2 and H_2 and removing NH_3 by liquefaction as it is formed, causing the unreacted N_2 and H_2 to form more ammonia. The presence of a catalyst helps the hydrogen and nitrogen molecules interact to form ammonia more rapidly.

Equilibrium constants are dependent upon the temperature of the system. Formation of ammonia is exothermic—heat is released as the reaction occurs: $N_2 + 3H_2 \rightleftarrows 2NH_3 + 93.7$ kilojoules of energy. Therefore, cooling the reaction mixture favors the formation of even more ammonia.

Systems may be in chemical or mechanical equilibrium, and they may also exhibit thermal equilibrium. If a hot object is placed in contact with a colder mass of the same material inside an insulated container, heat flows from the hot object into the colder object until the temperatures of the two are equal. Heat lost by the warm object is equal to the amount gained by the cold object. The amount of heat needed to raise the temperature of an object a certain amount is equal to the amount which that object would lose in cooling by the same amount. The amount of heat needed to warm or the amount lost when cooling equals the product of the specific heat (or heat capacity) of the substance, the mass, and the change in temperature. For example, if a 50-gram (1.8-ounce) piece of silver at 70°C (158°F) is placed in 50 grams (1.8 ounces) of water at 15°C (59°F), the principle of thermal equilibrium can be used to calculate the final temperature of the water and silver:

$$K_{eq} = \frac{[HI]^2}{[H_2]\ [I_2]} = 50$$

At equilibrium, if the concentrations of hydrogen and iodine were 1.0 mole/Liter, the concentration of hydrogen iodide would be $\sqrt{50}$ or 7.1 moles/Liter.

As a result of heat flowing from the silver into the water to establish a thermal equilibrium between the two, the final temperature of the silver and water is 18.1°C (64.6°F). SEE ALSO Chemical Reactions; Thermodynamics.

Dan M. Sullivan

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isotope: form of an atom that differs by the number of neutrons in the nucleus

Erbium

MELTING POINT: **1,529°C**
BOILING POINT: **2,510°C**
DENSITY: **9.07 g cm^{-3}**
MOST COMMON ION: **Er^{3+}**

Er
68
167.26

Erbium is a chemical element. Its ground state electronic configuration is [Xe]$4f^{12}$ $6s^2$. Natural erbium is a mixture of six stable **isotopes**. Monazite and xenotime are the principal erbium ores, in which erbium occurs together with other members of the **rare earth elements**, or the **lanthanides**. It can be separated from the other rare earths by ion exchange or solvent extraction techniques. The discovery of erbium is attributed to Carl G. Mosander (1842). Its name is derived from Ytterby, a small town in Sweden, where the first rare earth mineral (gadolinite) had been found. The elements ytterbium, yttrium, and terbium have also been named after the town of Ytterby.

rare earth elements: older name for the lanthanide series of elements, from lanthanum to lutetium

lanthanides: a family of elements from lanthanum to lutetium having from 1 to 14 4f electrons

Pure erbium **metal** was first prepared in 1934. It is a silver-white, malleable, and **ductile** metal. The metal is not oxidized as rapidly as other rare earth metals when exposed to air. Erbium chemistry is dominated by the trivalent erbium(III) ion, Er^{3+}. Its chemical behavior resembles that of yttrium and the heavy rare earth elements. The ground state electronic configuration of Er^{3+} is $[Xe]4f^{13}$. Because of erbium's narrow absorption band in the green region of visible light (at wavelengths of ca. 530 nanometers, or 2.09×10^{-5} inches), erbium(III) salts are pink. Due to the high chemical stability of trivalent erbium, erbium(III) oxide is used to color glassware pink. Erbium is of importance to the technology of optical amplification in glass fibers. Erbium-doped crystals can be used to generate laser beams having wavelengths in the vicinity of 2,900 nanometers (1.14×10^{-4} inches). Such lasers are being used in laser surgery. The laser beam is strongly absorbed by water, so that the energy in hitting its target is confined to the surface layer of tissue. Phosphors based on erbium can convert infrared light to visible light (upconversion). SEE ALSO CERIUM; DYSPROSIUM; EUROPIUM; GADOLINIUM; HOLMIUM; LANTHANIDES; LANTHANUM; LUTETIUM; NEODYMIUM; PRASEODYMIUM; PROMETHIUM; SAMARIUM; TERBIUM; YTTERBIUM.

metal: element or other substance the solid phase of which is characterized by high thermal and electrical conductivities

ductile: property of a substance that permits it to be drawn into wires

Koen Binnemans

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Estrogen

Estrogen is not one hormone, it is the name used to denote either of two steroid hormones. These hormones are noted for their role in the development of the secondary sexual characteristics of females. In mammals the most abundant (and most potent) estrogen is estradiol (a **dialcohol**: note the "-diol" suffix), followed by estrone (a **ketone**: note the *-one* suffix). As is true for the other steroid hormones, the major **biosynthetic** pathway for estrogen begins with cholesterol (C_{27}). The figure shows the major metabolic **intermediates** in the usual **synthesis** of estrogen, starting with cholesterol, proceeding to pregnenolone (C_{21}), an **androgen** (C_{19}), and then estrogen (C_{18}). Estrogen has an alcohol **functional group** at the C3 and C17 positions, and a methyl group at C13. A unique aspect of estrogen biosynthesis is the conversion (catalyzed by the enzyme aromatase) of the A ring to an aromatic ring.

Estrogen is produced in the ovaries and secreted into the blood, whereupon it enters target cells throughout the body. It enters the cells via **passive diffusion** and binds to specific proteins called estrogen **receptors**,

dialcohol: organic molecule containing two covalently bonded –OH groups

ketone: one of the characteristic groups of atoms in organic compounds that undergoes characteristic reactions, generally irrespective of where it occurs in the molecule; the FC(O)R functional group

biosynthesis: formation of a chemical substance by a living organism

intermediate: molecule, often short-lived, that occurs while a chemical reaction progresses but is not present when the reaction is complete

synthesis: combination of starting materials to form a desired product

androgen: group of steroids that act as male sex hormones

functional group: portion of a compound with characteristic atoms acting as a group

passive diffusion: mechanism of transporting solutes across membranes

receptor: area on or near a cell wall that accepts another molecule to allow a change in the cell

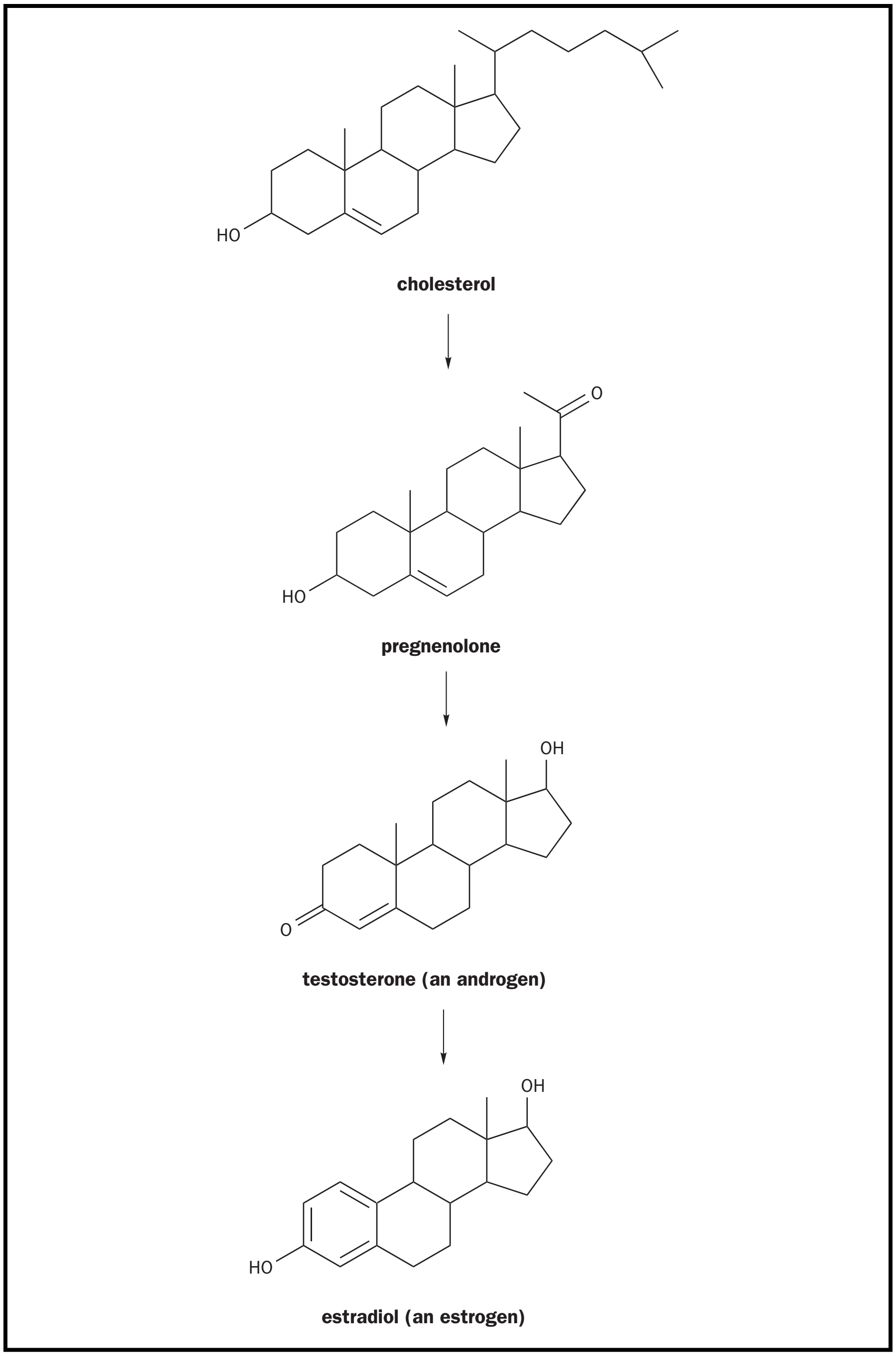

Figure 1. Major steroids in the synthesis of estrogen from cholesterol.

which reside in the cell nuclei. In the absence of estrogen, these receptors are functionally inactive. The binding of estrogen to a receptor activates the receptor, which can then bind to specific sites on the **DNA** to stimulate the **transcription** of a highly specific set of genes. As a result, the **metabolism** and the character of the cell changes.

In addition to its role in the development of the secondary sex characteristics in females, estrogen has important physiological functions in the cardiovascular, immune, and central nervous systems, as well as its effects on the growth and maturation of the long bones. It is also implicated in a number of diseases (including breast and uterine cancers) and in

DNA: deoxyribonucleic acid—the natural polymer that stores genetic information in the nucleus of a cell

transcription: enzyme-catalyzed assembly of an RNA molecule complementary to a strand of DNA

metabolism: all of the biochemical processes that take place within living organisms; comprises processes that produce complex substances from simpler components, with a consequent use of energy (anabolism), and those that break down complex food molecules, thus liberating energy (catabolism)

EDWARD DOISY (1893–1986)

Before Edward Doisy earned the Nobel Prize for his research on vitamin K, he studied female hormones. It was at this time in 1936 that he isolated estradiol. In rodents without ovaries, small injections of this isolated compound were able to replicate the same behavior and biological processes as if the ovaries were still present.

—Valerie Borek

postmenopausal health problems, such as atherosclerosis, osteoporosis, and diminution of cognitive functions. Because these conditions, especially female cancers, are associated with estrogen, a number of anticancer treatments involve estrogen blockade: drugs that prevent estrogen from binding to its receptors. As a result, the receptors remain in an inactive form. SEE ALSO Steroids.

William M. Scovell

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Ethics

Chemistry, like any discipline, has a social structure. It relies on the interactions, behaviors, and expectations of individuals in order to function. Every social structure has a code of practices that constitutes its behavioral norms, that is, a set of rules governing what are acceptable and unacceptable behaviors. These rules are the moral philosophy of that social structure. When people find themselves in a situation in which there is a conflict or dilemma, the decision-making processes that they use to make the behavioral choices that follow are called ethical decision-making skills. Ethics, then, is the process whereby an individual, faced with a moral dilemma, arrives at a morally defensible decision.

What do these ideas have to do with science? The answer is that science as an undertaking is a quite human process that relies on many decisions. For example, progress in science relies on the complete honesty of those who report their experimental results, because (among other reasons) those results are key to the understanding of the natural phenomena under investigation. In addition, because scientific results are generally made public and accessible to all, it is extremely important that scientific results are trustworthy. If results are not reported honestly, then anyone who uses these results in his or her work has had his or her trust violated, and the injured party has wasted time and other resources. When the results impact a field such as medicine, or bear on product safety, an immense number of people could be put in harm's way because of decisions made on the basis of false information.

A scientist's past experience of ethical decision making is embedded in every value judgment he or she makes, large and small. Aspects of scientific enterprise that require ethical decision making encompass a broad range of responsibilities, including experiment design, the interpretation and report-

Stem cell research, a recent technological advance in which cells are grown to generate new tissue, has the scientific community facing new ethical issues.

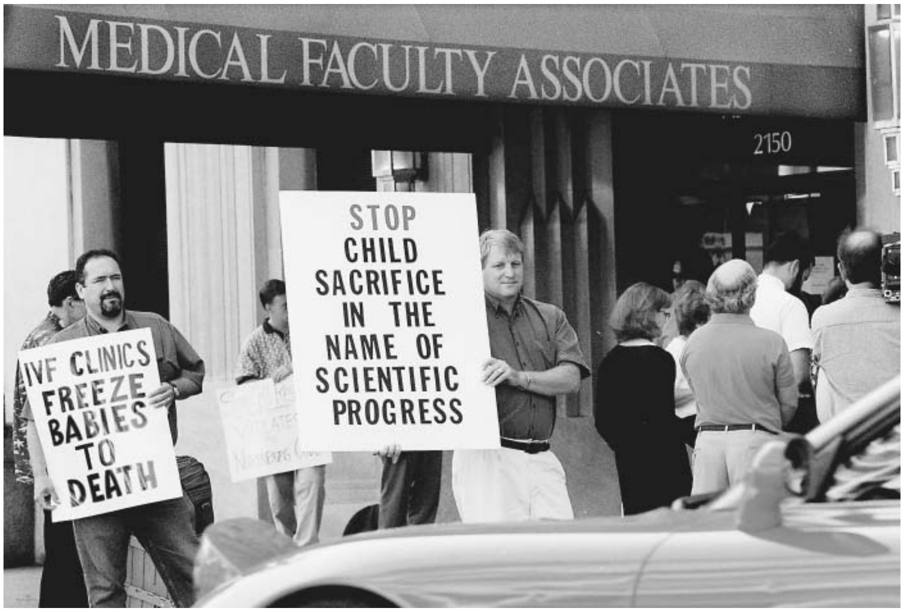
ing of data, interactions between collaborators, and the evaluation of colleagues.

When a scientist "cheats" for any reason, for instance by making up results or excluding selected data, the entire process of science is shaken. Other scientists and laypeople will make decisions based on the false reports that are generated, and these decisions could have devastating consequences. Imagine someone overseeing a clinical trial designed to test a medical treatment not disclosing a harmful side effect. Also imagine that people might actually be harmed because of such a nondisclosure. There are many reasons why a scientist might choose not to disclose potentially hurtful information. Perhaps he or she stands to make a financial profit from the sale of this medical treatment. Perhaps he or she is being pressured by a supervisor to report false results and is under threat of being fired. Personal gain at the expense of others is often the crux of willful misrepresentation of scientific experiments.

The use of human and animal subjects in drug testing is an area in which scientists must practice ethical reasoning in order to explore complex and contradictory ideas. There are all sorts of views held by all sorts of people on whether drug testing should be conducted on living beings. It is important for scientists to consider the moral philosophies that underlie these different perspectives, as they will have to make the decisions to proceed (or not) with such testing. Apart from the responsibilities of scientists, a nonscientist must sometimes decide, for example, whether she or he wants to be part of an organization that participates in such testing.

Topical Categories

Some ethical reasoning topics have been well debated over time, although every new technological advance spawns a new set of debates (for example, debates having to do with the uses of genetic information or research



Demonstrators outside George Washington University Hospital, Washington, D.C., protesting embryonic stem cell research.

involving stem cells). A violation of the standards of ethical scientific practice is called scientific misconduct. Some major categories of scientific misconduct, as outlined by the U.S. Department of Health and Human Resources, are:

- *Falsification of data.* Data fabrication (creating data that never existed). Selective reporting of findings. Omission of data that conflicts with other data (leaving out information in order to make one's story seem better). Willful suppression of data (not revealing relevant information) and/or distortion of data (exaggeration, for example).
- *Plagiarism.* Stealing the language, ideas, or thoughts of another and representing them as one's original work.
- *Improprieties of authorship.* Giving credit improperly or not giving credit at all in published materials. Publishing the same results in more than one place and claiming that each is an exclusively published report. Listing as authors individuals who have not made a definite contribution to the work published. Submission of multiauthored manuscripts to publishers without the agreement of all authors on the content of the text.
- *Misappropriation of the ideas of others.* An important aspect of scholarly activity is the exchange of ideas among colleagues. New ideas gleaned from such exchanges can lead to important discoveries. Scholars also acquire new ideas during the review of grant applications and scientific manuscripts. Improper use of information acquired in these ways could constitute fraud. Wholesale stealing of such material constitutes scientific misconduct.
- *Violation of generally accepted research practices.* Serious deviation from accepted practices in proposing or carrying out research. Any manipulation of experiments to bring about desired results. Deceptive statistical or analytical manipulation of results or improper reporting of results.

- *Material failure to comply with federal requirements affecting research.* Includes but is not limited to serious or substantial, repeated and/or willful violations involving the use of funds, care of animals, human subjects, investigational drugs, genetic products, new devices, or radioactive, biologic, or chemical materials.
- *Inappropriate behavior in relation to misconduct.* An inappropriate accusation of misconduct. Failure to report known or suspected misconduct. Withholding or destroying information relevant to a claim of misconduct. Retaliation against any person taking part in the allegation or investigation.
- *Deliberate misrepresentation of qualifications, experience, or research accomplishments (one's own or another's) to advance a research program, to obtain external funding, or to further other professional advancement.*
- *Misappropriation of funds or other resources.* For example, use of funds for personal gain.

An Example from Practice

The reproducibility of results is a hallmark of establishing reliable knowledge in scientific practice. In 2000 Professor Gérard Buono reported the results of a series of experiments carried out by him and his coworkers in France (Buono et al. 2000, p. 2554). In late 2001, Buono published a retraction of these results (Buono 2001, p. 4536). The retraction and accompanying story recounted in the text are an example of the self-correcting nature of ethical scientific practices. Buono describes how he was contacted by the editor of the journal that published the results and by Professor Scott E. Denmark, a scientific leader in the relevant area of chemistry who had not been able to reproduce the experimental results. In his retraction Buono writes, "At this stage, I asked my co-workers to check the experimental procedures and analytical conditions and to try to reproduce the described results. I was provided with experimental data and material that fully confirmed our original claims." After repetition of the experiments and upon close examination of his students' work, however, Buono saw evidence of error. He writes that he "noticed several inconsistencies with the analytical material the students had previously provided. Therefore, I decided to reproduce *personally* and *independently* the whole experimental procedures from the very beginning." Buono could not reproduce the results originally reported by him and his coworkers, but obtained the results reported by Denmark and his coworkers. Buono concluded this episode by writing that he wished "to withdraw [the original] communication. Other pieces of work based on related experimental results that were published elsewhere will also be withdrawn."

A Moral Education

Where and how do students learn about these ethics-related scientific practices? Historically, for scientists in training the process has been rather learn-as-you-go. It is generally assumed that senior scientists and teachers follow a code of defensible moral behavior and that, by their example, valuable lessons are transmitted to their students. Unfortunately, these assumptions are not necessarily valid, and cases of scientific misconduct surface in the news fairly regularly. By making ethical reasoning and the expectation of moral scientific behavior a more explicit part of education, it is hoped that the number of such cases can be reduced. The strategies for making rules of conduct explicit vary, and it is also hoped that many messages from many sources will impact the way scientists and future scientists make decisions.

In 1994 the editors of the Publications Division of the American Chemical Society (ACS) began publishing a series of articles titled "Ethical Guidelines to Publication of Chemical Research" in ACS journals. (See, for example, the *Journal of the American Chemical Society* [1994] 116[13]: 8A–10A.) These guidelines, revised in January 2000, define the ethical obligations of each participant in the science community who is responsible for bringing a scientific publication to that community, namely, the editors, authors, reviewers, and scientists publishing in the more popular science venues. As stated in the introduction to these guidelines, one characteristic of a profession is for its members to have an accepted code of behaviors, responsibilities and obligations, to one another and to the public. The advancement of science requires sharing information in an utterly honest and open fashion. Editors need to give unbiased consideration to all scientific reports submitted for publication in a timely and fair manner. Those who have the privilege of reviewing unpublished scientific results cannot use or disclose that information prior to its publication. Reviewers must also be sensitive to conflicts of interest; for example, a reviewer should not review a manuscript if it is authored by a person with whom the reviewer has a close personal relationship, or a relationship which would otherwise bias the reviewer's ability to judge the manuscript fairly. Authors are obliged to provide an accurate and honest account of their work, with enough information so that reviewers and readers can properly evaluate the validity of the information and reproduce the results.

In scientific research, as in business and medicine, the writing of and analysis of case studies are an effective formal vehicle for ethics instruction. Students, having been given an authentic narrative scenario to consider and debate, can practice ethical reasoning as they think through the moral issues that have been raised by a particular case. A case study debated in a classroom is a safe proceeding, because it is not an actual circumstance in which a student might face serious personal consequences. Educators hope that students, having to think through ethics-related dilemmas in classroom settings, can acquire the reasoning skills they are going to need when they are confronted with actual situations. The following is an excerpt from a case study.

> After only a few days in your new lab, you notice that one of the senior students is quite open about what appear to be many questionable experimental practices: he does not really keep a notebook, but numbers a new page for each reaction he performs and scribbles out a little information about what he had done, sometimes only the date and the starting time. . . . By now, his practices are quite well known in your particular lab room, and a number of jokes and asides by your labmates affirm your perceptions. Indeed, even the senior student has been heard to quip: "If I had done this the right way, I think the yield would have been 75%." When the research advisor comes to lab for a weekly update on progress, this student presents the data on the purified materials and reports a 75% yield. The research advisor and this student

> have already published 3 papers based on his previous results. Who is potentially affected by this student's behavior? What are your options for possible actions? (Coppola, pp. 1506–1511)

It is important to understand that the educative development of ethical reasoning skills neither represents nor advocates a prescribed moral position, and does not commit a student in advance to dogmatic solutions to all moral problems. Ethics, or ethical reasoning, is the process by which the most defensible resolution to a moral dilemma is sought.

Brian P. Coppola

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Europium

MELTING POINT: 1,099K
BOILING POINT: 1,800K
DENSITY: 5,244/kg m^{-3}
MOST COMMON IONS: Eu^{3+}, Eu^{2+}

63
Eu
EUROPIUM
151.97

Europium is a metallic element discovered in 1901 in Paris by the French scientist Eugène-Anatole Demarcay. It belongs to a series of elements called **lanthanides**, or 4f elements, extending from lanthanum (atomic number 57) to lutetium (atomic number 71). These elements have low abundances: Europium occurrence in Earth's crust is only 2.1 ppm (parts per million), that is, 2.1 grams (0.07 ounces) per metric ton, and in seawater, its concentration is as low as 4×10^{-8} ppm.

lanthanides: a family of elements (atomic number 57 through 70) from lanthanum to lutetium having from 1 to 14 4f electrons

As a **metal**, europium is very reactive so that one usually finds it under its trivalent, triply oxidized form (Eu^{3+} ion) in oxides or salts. A divalent form (Eu^{2+}) also displays some stability. Two minerals that contain many of the lanthanide elements, which are separated by liquid-liquid extraction, are commercially important: monazite (found in Australia, Brazil, India, Malaysia, and South Africa) and bastnasite (found in China and the United States).

metal: element or other substance the solid phase of which is characterized by high thermal and electrical conductivities

A very interesting property of the europium ions is their bright red (Eu^{3+}) and bright blue (Eu^{2+}) luminescence. The red luminescence has been instrumental in identifying the element and it is of great practical use today. For instance, the red color seen on computer and television screens derives from red light emitted by a europium-containing phosphor (an inorganic compound with 4–7% Eu^{3+}). The same type of material is used in energy-saving fluorescent lamps: Those displaying a warm light contain Eu^{3+}. In medicine, **antibodies** (molecules generating an antibody response, e.g., certain hormones) labeled with a europium-containing compound react with specific antigens, forming antigen-antibody complexes, and the red luminescence helps to quantify these hormones in biological fluids (e.g., blood, urine). SEE ALSO CERIUM; DYSPROSIUM; ERBIUM; GADOLINIUM; HOLMIUM; LANTHANIDES; LANTHANUM; LUTETIUM; NEODYMIUM; PRASEODYMIUM; PROMETHIUM; SAMARIUM; TERBIUM; THULIUM; YTTERBIUM.

antibody: protein molecule that recognizes external agents in the body and binds to them as part of the immune response of the body

Jean-Claude Bünzli

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Explosions

An explosion is a sudden, violent change of potential energy to work, which transfers to its surroundings in the form of a rapidly moving rise in pressure called a blast wave or shock wave. The shock wave can cause substantial damage. Potential energy may exist in either of three forms before an explosion occurs: **nuclear**, chemical, or physical. Generally, nuclear explosions are much larger and more destructive than chemical or physical explosions. Chemical explosions are more frequent than nuclear or physical explosions. Although chemical explosions are usually deliberate, they may also occur accidentally. Large physical explosions are relatively rare and usually accidental.

nuclear: having to do with the nucleus of an atom

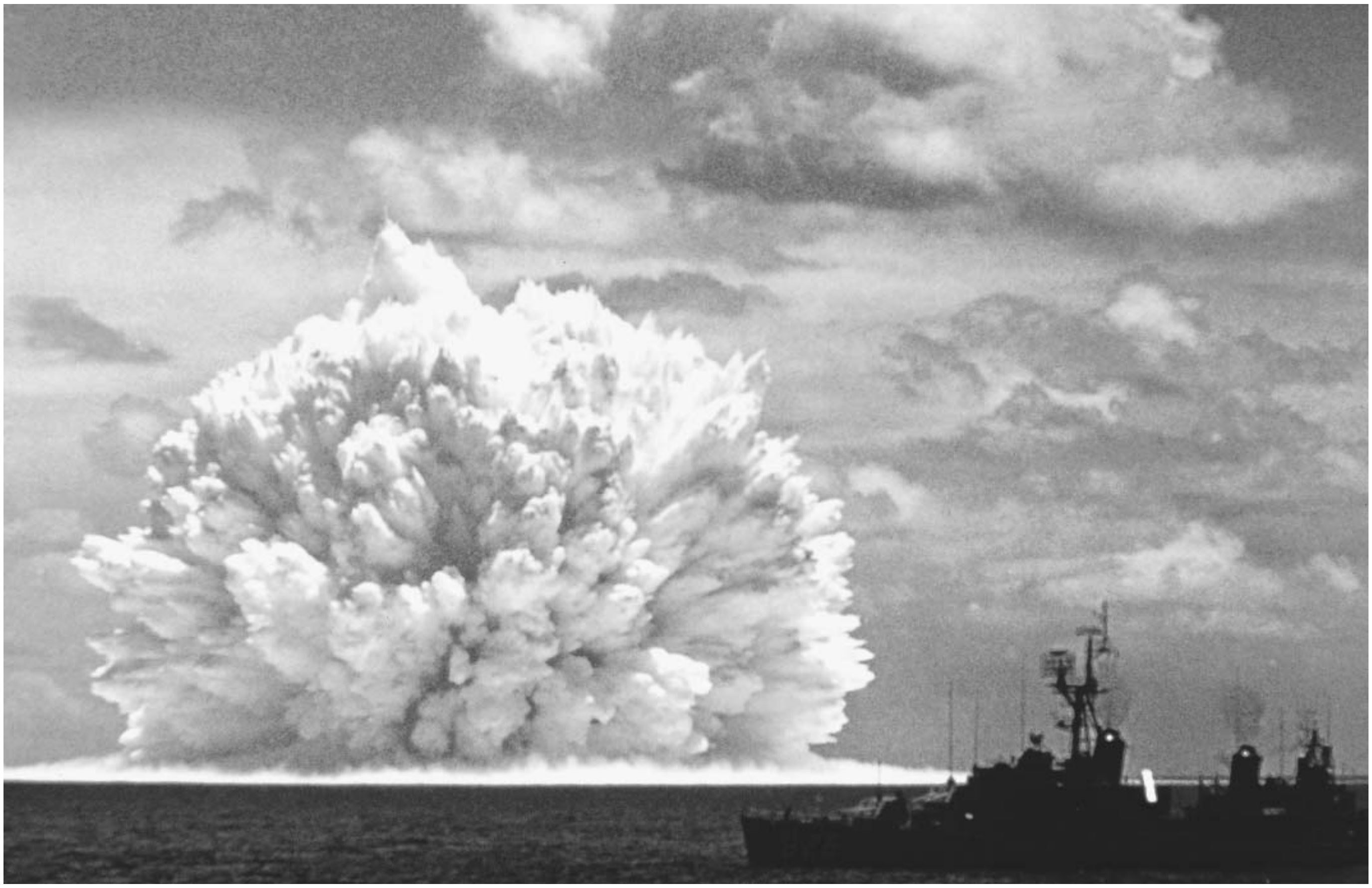
Nuclear Explosions

Nuclear explosions may be caused by either fusion or **fission** reactions. In a **fusion** reaction, the nuclei of two small atoms combine to form a single larger atom, sometimes accompanied by a neutron. The mass of the products of the reaction is less than the mass of the reactants, and that difference in mass is converted to energy according to Einstein's well-known equation $E = mc^2$ where E is the energy produced, m the mass converted to energy, and c the speed of light. The speed of light is very large, and only a small amount of mass must be converted to result in a significant explosion.

fission: process of splitting an atom into smaller pieces

fusion: process of releasing nuclear energy by combining lighter elements such as hydrogen into heavier elements

In a fission reaction, a single large atom, such as uranium, is bombarded with neutrons, causing the nucleus of the atom to split into two smaller nuclei and several neutrons. The combined mass of the product atoms and neutrons is less than the mass of the original atom, and the mass loss is converted to energy according to Einstein's equation. The neutrons produced by the fission reaction cause other large atoms to fission, and their neutron production causes still other atoms to fission, leading to a chain reaction that continues exponentially (i.e., 2, 4, 8, 16, 32, 64 . . .). The entire process is very rapid, taking only a few millionths of a second. The resulting energy production heats the surrounding air and causes it to expand in the form of a blast wave.



A nuclear explosion at sea.

Both fusion and fission reactions can be used in bombs. The fusion reactions require a very high temperature to get started, so they are initiated by fission reactions. (When controlled at slower rates in nuclear reactors, fission reactions are used to produce power and additional nuclear fuel.)

Chemical Explosions

Chemical explosions may be either decomposition or combination reactions. In either case, the reaction is exothermic and the energy released by the reaction is partially converted to work. Decomposition reactions occur in materials such as trinitrotoluene (TNT) and nitroglycerine. The molecules of these materials contain oxygen. When the molecule decomposes, the products are **combustion** gases, which are produced at high temperatures. The volume of the gases is much larger than the volume of the explosive, generating high pressures at the reaction zone. The rapid expansion of the gases forms the shock wave that provides the explosive effect. Even some hydrocarbons that have no oxygen in their molecules, such as acetylene, can decompose explosively.

combustion: burning, the reaction with oxygen

Combination reactions require that two or more components react together exothermically to produce hot gases. Some examples are ammonium nitrate and fuel oil (ANFO), gunpowder (potassium nitrate, carbon, and sulfur), and fireworks. In these explosions, the reactants that make up the explosive must be carefully mixed to assure that the reaction will continue.

The damage caused by an explosion depends partly on how fast the explosive reaction occurs. Decomposition reactions generally occur much faster than combination reactions. They are more likely to be used for military applications because they are more destructive. They also have a stronger shattering effect (called brisance) than combination reactions. Combination explosions are frequently used in mining operations because they have lower brisance and occur at slower rates.

There is a special case of explosion known as a vapor cloud explosion that can occur when a fuel (such as ordinary propane) is mixed with the atmosphere. If the cloud is ignited, the burning rate may be fast enough to form a shock wave. Although the overpressure in the shock wave may not be very high compared to other explosions, it is strong enough to damage or destroy structures. In a vapor cloud explosion, the result is called a deflagration if the shock wave moves slower than the speed of sound and a detonation if the shock wave moves faster than the speed of sound. Detonations are more destructive than deflagrations because of their stronger shock waves.

It should be kept in mind that explosives are generally unstable compounds. Once the exothermic decomposition or combination reaction is started, the temperature rises and the reaction accelerates; it usually cannot be stopped.

Physical Explosions

Physical explosions are those in which no chemical or nuclear reaction occurs. The most frequent example is the rupture of a vessel whose contents, either gas or liquid, exist under high pressure. If the containing vessel bursts, its contents are free to expand and a shock wave is formed. Even a common automobile tire can explode if it is highly overinflated.

Liquids that have a normal boiling point well below ambient temperatures are sometimes stored (under their own vapor pressure) at pressures well above atmospheric pressure. If the tank holding the liquid bursts, part of the liquid vaporizes extremely rapidly and expands, forming a shock wave. This process is called a boiling liquid expanding vapor explosion (BLEVE) and the resulting explosion can be very destructive.

Explosions can be used for constructive purposes, such as mining and road building; for entertainment, such as fireworks; or for destructive purposes, such as military weapons and terrorist bombs. They may be either deliberate or accidental. Explosive materials must always be handled with extreme care to prevent accidents. Such caution must be exercised with not only industrial explosives, but also commonly encountered materials such as fireworks, laboratory and industrial chemicals, and flammable gases. SEE ALSO FIRE, FUELS, POWER PLANTS; FIREWORKS; KINETICS; NUCLEAR FISSION; NUCLEAR FUSION; THERMODYNAMICS.

J. Reed Welker

Fahrenheit, Daniel Gabriel

GERMAN PHYSICIST
1686–1736

Observations are the heart of the scientific method, but human perception is faulty when it comes to observing “absolutes.” That is, one may be able to say that this liquid is hotter than that liquid, but not by how much, nor their exact temperatures. For science to be meaningful and its results reproducible, some external mechanism for making (and comparing) measurements that can be used by scientists must exist.

Daniel Gabriel Fahrenheit was a German physicist living in the Netherlands in the early eighteenth century. Like many of his contemporaries, he was interested in a great many phenomena, but the one phenomenon that really seized his attention was the boiling of liquids. Fahrenheit discovered that pure liquids boil at fixed temperatures, which are not influenced by the continued application of heat. He described his reaction to this discovery in his *Philosophical Transactions* (1724): "I was at once inflamed with a great desire to make for myself a thermometer of the same sort [a water-based thermometer], so that I might with my own eyes perceive this beautiful phenomenon of nature, and be convinced of the truth of the experiment."

Fahrenheit could not make a "thermometer of the same sort," despite repeated attempts. The type of thermometer that he was trying to make used water, open to the atmosphere, as the fluid of expansion. His original thermometers were thus sensitive to air pressure, and acted as both barometers and thermometers at the same time.

Fahrenheit subsequently recognized that both alcohol and mercury expanded with heat. He built closed bulb thermometers that contained alcohol (1709) and mercury (1714), thereby inventing the modern thermometer. With these instruments, he was able to make much more accurate and more consistent measurements of temperature. And he discovered, among other things, that water can be supercooled (cooled below its normal freezing point), and that the boiling point of a liquid is not a constant, but is a function of atmospheric pressure. Fahrenheit used supercooled water (from a mixture of water, ice, and sal ammoniac [ammonium chloride]) to establish his zero point, and his own body temperature to establish what would be 100 degrees. (Of course, we now gauge normal body temperature to be 98.6°F.) Fahrenheit's thermometers were the first to enable accurate and reproducible measurements of temperature.

Until the 1970s, the Fahrenheit scale was in common use in all English-speaking countries. Since then, the Celsius scale has been adopted by most countries (not including the United States). SEE ALSO TEMPERATURE.

Todd W. Whitcombe

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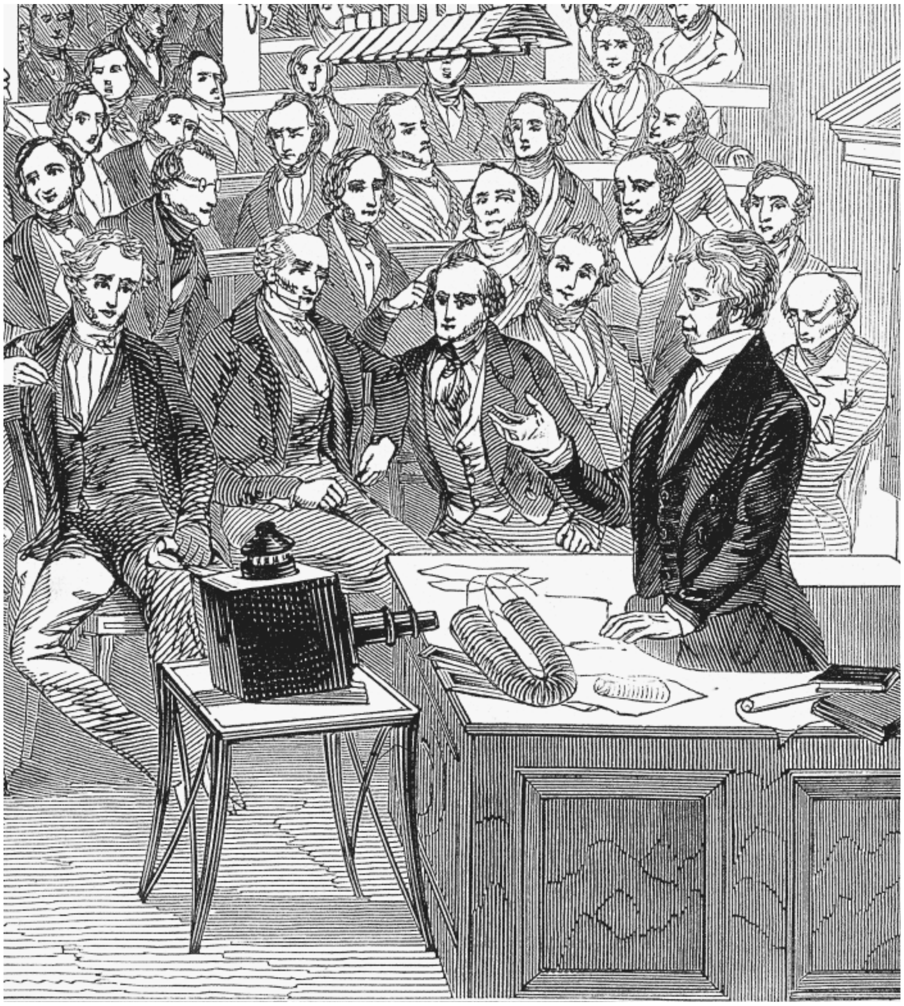
Faraday, Michael

ENGLISH CHEMIST AND PHYSICIST
1791–1867

Michael Faraday, the leading chemist and natural philosopher in England during the middle third of the nineteenth century, discovered the principle behind the electric motor (1821), benzene (1825), the electric transformer



English chemist and physicist Michael Faraday, who developed the field theory of electromagnetism.

and generator (1831), the laws of electrolysis (early 1830s), and the magneto-optical effect and diamagnetism (1845), which enabled him to develop the field theory of electromagnetism, one of the cornerstones of modern physics.

Faraday was born on September 22, 1791, in Newington Butts, south of London. His father, a blacksmith, belonged to the Sandemanians, a small literalist sect (in which the members believe in the literal truth of the Bible) of Christianity. Faraday was fully committed to this sect, becoming a deacon in 1832 and an elder in the 1840s and again in the 1860s. He married a fellow Sandemanian, Sarah Barnard, in 1821 and died on August 25, 1867, in his "grace and favour" house (a house given by a monarch to a subject in recognition of worth and of need) at Hampton Court. In his scientific research, Faraday sought to determine the laws of nature that he believed God had written at the creation of the universe. Although it was only toward the end of his life that problems began to emerge between some types of Christianity and science, mostly in response to Charles Darwin's theory of natural selection, published in 1859, Faraday did not see any conflict between them.

Faraday attended a day school and in 1805 he began an apprenticeship as a bookbinder, which was to last for seven years. During this time he developed a strong interest in science, particularly chemistry, and in 1812, the final year of his apprenticeship, he attended four lectures delivered by Humphry Davy at the recently founded (1799) Royal Institution in London's West End. Faraday sent his notes on Davy's lectures to Davy asking for a job in the field of science; he was eventually appointed as an assistant in the Royal Institution's laboratory. Between the fall of 1813 and spring of 1815 he toured Europe with Davy and helped him establish the fact that iodine was a chemical element. Returning to England, Faraday was reappointed to the Royal Institution and promoted through the ranks, becoming the director of its laboratory in 1825 and first Fullerian Professor of Chemistry in 1833. In these roles, Faraday established Christmas lectures for children and Friday evening discourses, both of which series still continue.

During the 1820s much of Faraday's work centered on chemistry. He aided Davy in his disastrous efforts to protect electrochemically the copper bottoms of ships and with the equally unsuccessful project to improve optical glass. In 1823 Faraday liquefied the gas chlorine for the first time and in the 1840s he liquefied several more gases. His **liquefaction** of chlorine resulted in a bitter break with Davy, by now president of the **Royal Society**, who believed that Faraday had not given him sufficient credit for his part in the work. Davy thus tried, albeit unsuccessfully, to block Faraday's election to the Royal Society. Two years later Faraday discovered, but did not investigate fully, a new chemical that he named "bi-carburet of hydrogen." Nearly ten years later Eilhardt Mitscherlich, a chemistry professor in Berlin, first undertook a detailed study of the substance that he renamed benzene. Faraday, nevertheless, is credited with benzene's discovery, and in 1925 there were major celebrations throughout England marking the 100-year anniversary of Faraday's discovery.

liquefaction: process of changing to a liquid form

Royal Society: The U.K. National Academy of Science, founded in 1660

Following his 1831 electromagnetic work, Faraday turned his attention to electrochemistry. The decomposition of chemical compounds was a standard test for the presence of electricity. In his extensive use of this test, he observed phenomena contradicting Davy's theory that electrochemical decomposition occurred at the **metal** pole. Faraday found that decomposition occurred in the substance itself and the poles did not need to be metal. All this led Faraday to develop a new language of electrochemistry. With a number of classical scholars, notably William Whewell, Faraday introduced terms such as electrolysis, electrolyte, electrode, anode, cathode, and ion (although he said there would be little need for this last term).

metal: element or other substance the solid phase of which is characterized by high thermal and electrical conductivities

Faraday was thus able to enunciate his two laws of electrolysis. His second law implied that both matter and electricity were atomic in nature. Faraday was deeply opposed to atomism, especially the theory proposed by John Dalton, and indeed held a very antimaterialist view. It was clear to Faraday, however, that the law of definite proportions also required some sort of **atomic theory**. What Faraday proposed in the 1840s was that matter was perceived where lines of force met at a particular point in space. A direct experimental outcome of this radical theory was Faraday's discovery in 1845 of the magneto-optical effect and diamagnetism. The field theory that Faraday developed from this was able to solve a number of problems in physics that were not amenable to conventional approaches. This was one reason why field theory was taken up quite quickly by elite natural philosophers such as William Thomson (later Lord Kelvin) and James Clerk Maxwell.

atomic theory: concept that asserts that matter is composed of tiny particles called atoms, the particular characteristics of which determine the form and type of matter.

Nevertheless, the theory was not generally accepted for some time because it was seen by many physicists as opaque and, in origin, nonmathematical. However, as the German organic chemist Justus von Liebig pointed out, this occurred because physicists did not recognize Faraday's background as a chemist, a factor Liebig thought crucial in the development of Faraday's theory: "To physicists, who have approached physics by the road of chemistry, Faraday's memoirs sound like admirably beautiful music" (Hofmann, p. 1100). SEE ALSO DALTON, JOHN; DAVY, HUMPHRY; ELECTROCHEMISTRY; IODINE; LIEBIG, JUSTUS VON; MAXWELL, JAMES CLERK.

Frank A. J. L. James

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Fats and Fatty Acids

Fats occur naturally in food and play a significant role in human nutrition. Fats are used to store energy in the body, insulate body tissues, cushion internal organs, and transport fat-soluble **vitamins** in the blood. Fats also play in an important role in food preparation: They enhance food flavor and food texture, make baked products tender, and conduct heat during cooking.

vitamins: organic molecules needed in small amounts for the normal function of the body; often used as part of an enzyme catalyzed reaction

Fats are the most prevalent class of compounds (in living systems) referred to as **lipids**. Lipids are cellular compounds that are insoluble in water. Fats are soft, low-melting solids, with a density less than that of water. They have a greasy feel and are slippery. Because fats are insoluble in water and less dense than water, after meat that has a lot of fat in it has been cooked, upon cooling a layer of fat often appears on top of the juices. Fats and closely related oils are mixtures of compounds consisting of fatty acids combined with glycerol (commonly known as glycerin) via **ester** linkages. Fatty acids are long, straight chain carboxylic acids. A fat (or oil) is formed when three fatty acid molecules react with a glycerol molecule to yield a triglyceride (and three water molecules). (See Figure 1.) Fats in the body are transported and stored as triglycerides.

lipid: a nonpolar organic molecule; fatlike; one of a large variety of nonpolar hydrophobic (water-hating) molecules that are insoluble in water

ester: organic species containing a carbon atom attached to three moieties: an O via a double bond, an O attached to another carbon atom or chain, and an H atom or C chain; the R(C=O)OR functional group

Fat molecules are characterized as monoglycerides, diglycerides, or triglycerides, depending on whether there are one, two, or three fatty acid chains present in the molecules. Fatty acids in nature generally have an even number of carbon atoms because they are synthesized in cells via successive

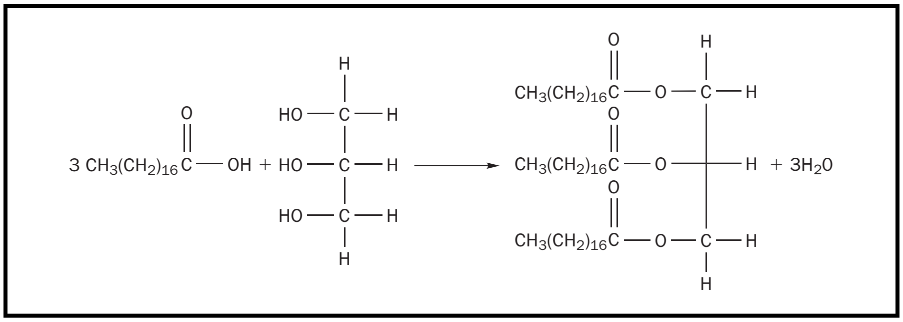

Figure 1. The formation of a triglyceride of stearic acid.

additions of two-carbon acetate groups in a stepwise cyclic reaction. Some fatty acids found in nature are shown in Table 1.

Fats and Oils

Dietary fats and oils are both triglycerides. Fats are generally solids and oils are generally liquids at ordinary room temperatures. The characteristics of fats and oils are related to the properties of the fatty acids that they contain. The larger the number of carbon atoms, the higher the **melting point**; the larger the number of double bonds, the lower the melting point. Oils contain a higher percentage of unsaturated fatty acids than fats. Fats from animal sources tend to be solids and fats from vegetable sources tend to be liquids. Thus fats are often referred to as "animal fats" and "vegetable oils."

melting point: temperature at which a substance in the solid state undergoes a phase change to the liquid state

When fats or oils are exposed to air, they react with the oxygen or water vapor to form short-chain carboxylic acids. The short-chain acids are **volatile** and have unpleasant smells and tastes. For example, the strong smell and sour taste of vinegar are due to acetic acid, a two-carbon **carboxylic acid**. The **oxidation** process is called rancidification and can make foods unpalatable. The characteristic smell of rancid butter is due to the presence of butyric acid (a four-carbon acid). (Rancidity can also be the result of the hydrolysis of fats or oils.)

volatile: low boiling, readily vaporized

carboxylic acid: one of the characteristic groups of atoms in organic compounds that undergoes characteristic reactions, generally irrespective of where it occurs in the molecule; the $-CO_2H$ functional group

oxidation: process that involves the loss of electrons (or the addition of an oxygen atom)

Unsaturated Fatty Acids

There are about forty naturally occurring fatty acids. The fatty acids without carbon-carbon double bonds are classified as saturated, and those containing carbon-carbon double bonds are classified as unsaturated. Palmitic and stearic acids are the most common saturated fatty acids, and oleic and linoleic acids are the most common unsaturated fatty acids. Oleic acid is monounsaturated because it has only one carbon-carbon double bond. Linoleic, linolenic, and arachidonic acids are polyunsaturated because they have two, three, and four carbon-carbon double bonds, respectively. A way to measure the relative degree of unsaturation of a fat or an oil is to determine its iodine number. The iodine number is the mass of iodine, in grams, that is consumed by (reacts with) 100 grams of a fat or an oil. Iodine reacts with the carbon-carbon double bonds. Thus the greater the number of double bonds, the higher the iodine number. In general, fats have lower iodine numbers than oils because oils have greater percentages of carbon-carbon bonds that are double bonds. For example, typical iodine numbers for butter are 25 to 40, and for corn oil, 115 to 130.

Table 1.

FATTY ACIDS

Common Saturated Fatty Acids

Number of Carbon Atoms	Formula	Common Name	Source
4	$CH_3(CH_2)_2COOH$	Butyric acid	Butter
6	$CH_3(CH_2)_4COOH$	Caproic acid	Butter
8	$CH_3(CH_2)_6COOH$	Caprylic acid	Coconut oil
10	$CH_3(CH_2)_8COOH$	Capric acid	Coconut oil
12	$CH_3(CH_2)_{10}COOH$	Lauric acid	Palm kernel oil
14	$CH_3(CH_2)_{12}COOH$	Myristic acid	Oil of nutmeg
16	$CH_3(CH_2)_{14}COOH$	Palmitic acid	Palm oil
18	$CH_3(CH_2)_{16}COOH$	Stearic acid	Beef tallow
18	$CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH$	Oleic acid	Olive oil
18	$CH_3(CH_2)_4CH{=}CHCH_2CH(CH_2)_7COOH$	Linoleic acid	Soybean oil
18	$CH_3CH_2(CH{=}CHCH_2)_3(CH_2)_6COOH$	Linolenic acid	Fish oils
20	$CH_3(CH_2)_4(CH{=}CHCH_2)_4(CH_2)_2COOH$	Arachidonic acid	Liver
22	$CH_3(CH_2)_{20}COOH$	Beheric acid	Sesame oil

Common Unsaturated Fatty Acids

Number of Carbon Atoms	Formula	Common Name	Source
16	$CH_3(CH_2)_5CH{=}CH(CH_2)_7COOH$	Palmitoleic acid	Whale oil
18	$CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH$	Oleic acid	Olive oil
18	$CH_3(CH_2)_4CH{=}CHCH_2CH(CH_2)_7COOH$	Linoleic acid	Soybean oil, safflower oil
18	$CH_3CH_2(CH{=}CHCH_2)_3(CH_2)_6COOH$	Linolenic acid	Fish oils, linseed oil
20	$CH_3(CH_2)_4(CH{=}CHCH_2)_4(CH_2)_2COOH$	Arachidonic acid	Liver

Hydrogenation

In addition to their reacting with iodine, unsaturated fats and oils react with hydrogen. Like iodine atoms, hydrogen atoms add across the carbon-carbon double bonds. Vegetable oils, with their higher degrees of unsaturation, can be converted to solids via reaction with hydrogen in a process called hydrogenation. A polyhydrogenated fat is one that has been altered by such a reaction. The reaction may cause the oil to become a solid. Margarine and shortening are vegetable-based oils that have undergone partial hydrogenation. Because the amounts of hydrogen added can be controlled, the products of these reactions can be engineered to have specific properties, such as degrees of softness and a chosen melting point. The peanut oil in peanut butter usually has been hydrogenated to prevent it from separating. Another product of partial hydrogenation is a class of fats called *trans* fatty acids. Foods high in *trans* fatty acids (for example, margarine, shortening, and commercially fried food) tend to raise cholesterol levels in the blood.

Composition of Fats and Oils

Fat and oil glyceride molecules can contain a single fatty acid species or any combination of up to three fatty acids. Most naturally occurring fat and oil molecules contain a combination of fatty acids. As indicated previously, the greater the percentages of carbon-carbon bonds that are double bonds

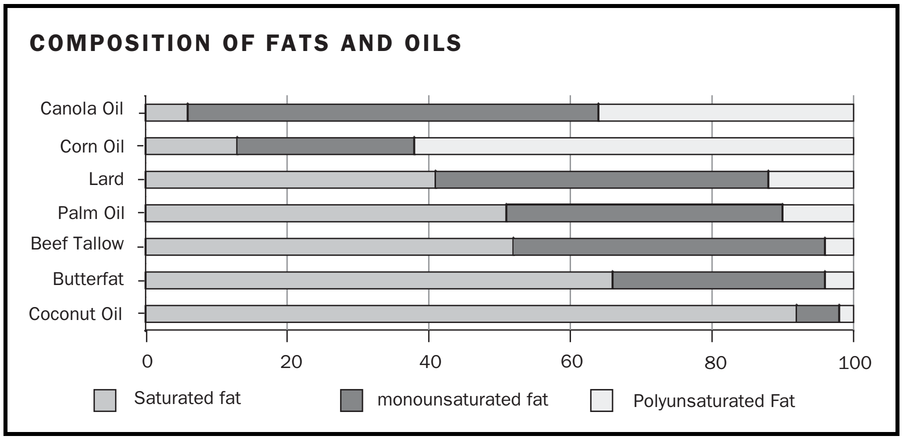

Figure 2.

in the fatty acids of a glyceride, the lower is the melting point and the more likely the glyceride will exist as a liquid at room temperature. Figure 2 shows the composition (in terms of their saturated, monounsaturated, and polyunsaturated portions) of some common fats and oils. Note that the oils tend to contain fewer saturated fatty acids. Coconut oil is an exception; although it does contain an ample amount of saturated fatty acids, approximately two-thirds of its fatty acid content is derived from lauric and myristic acids. Lauric and myristic acids have shorter chains of 12 and 14 carbons, respectively, and they are responsible for the low melting point of coconut oil.

Saponification

Because fats and oils are triesters of glycerol, they react with water to form fatty acids and glycerin. When the reaction is carried out in a basic solution, salts of the fatty acids are produced instead of the fatty acids themselves. The salts of fatty acids are soaps and an individual molecule is characterized by an ionic end (the salt part) and a **nonpolar** end (the hydrocarbon part). The ionic salt end is water-soluble and the nonpolar hydrocarbon end is water insoluble. The process of making soaps by treating fats and oils with basic substances is called saponification (which means "soapmaking"). Pioneers made soap by adding lye (the base sodium hydroxide) to animal fat, and then heating the mixture. The soap rose to the top of the pot and solidified upon cooling and the glycerol remained at the bottom.

nonpolar: molecule, or portion of a molecule, that does not have a permanent, electric dipole

Fats and oils can be characterized by their saponification numbers. The saponification number is defined as the number of milligrams of potassium hydroxide needed to saponify completely one gram of a fat or an oil. One mole of fat requires three moles of potassium hydroxide for complete saponification. If a fat contains fatty acids of relatively high molecular weights, then one gram of the fat will consist of fewer moles. Thus, fats having greater percentages of high molecular weight fatty acids will have lower saponification numbers than fats having greater percentages of lower molecular weight fatty acids. Lard, which contains mostly 16- and 18-carbon fatty acids, has a saponification number range of 190 to 200. Coconut oil, which is about 50 percent lauric acid, a 12-carbon fatty acid, has a saponification number approaching 260.

Fats in the Diet

Fats are necessary to maintain the body. Dietary fats exist mainly in the form of triglycerides. Fats are classified as high-energy food. They provide about 9 kilocalorie (kcal) of energy per gram consumed. In contrast, both carbohydrates and proteins provide about 4 kcal of energy per gram consumed. As a result, fat is the most efficient way to store energy. If one consumes more calories than he or she needs, some of the excess calorie source is converted to fat.

It is generally recommended that not more than 30 percent of one's dietary calories should derive from fat (and of this 30 percent, 10 percent should be monounsaturated, and 10 percent, polyunsaturated). It appears that consumption of greater amounts of saturated fats (compared to amounts of monounsaturated and polyunsaturated fats) is related to higher levels of cholesterol in the blood and a greater risk of heart disease. In the United States the average diet is about 34 percent fat and (13 percent saturated fat).

Fat Substitutes

Because an average American diet tends to be higher in fats than what is recommended, there have been quests for substitutes for fat. Three products were first marketed as fat substitutes in the 1990s. The first was Simplesse, made by G.D. Searle. It is a low-calorie fat substitute made from milk protein (whey). The whey is made to undergo a microparticulation process that produces microparticles and prevents the formation of larger particle aggregates. The small size and uniformly spherical shape of Simplesse particles are responsible for this product's resemblance to a creamy fluid. The texture of Simplesse is similar to that of fats, and its use in frozen desserts can inhibit the growth of ice crystals. Simplesse is used in cheeses, frozen desserts, dressings, spreads, and puddings. It cannot be used in foods that require baking or frying.

Another product is Olestra, made by Procter and Gamble, and it is sold to food producers as Olean. It is an ester of sucrose (instead of glycerol), and it is used as a substitute for fats in potato chips, crackers, and tortilla chips. Olestra's similarity to fats with respect to molecular structure contributes to its ability to mimic the mouth-feel of fat. However, it is much bulkier than a triglyceride-containing food, and this bulkiness prevents it from being digested and absorbed by the body. Thus it has no dietary caloric content. Potato chips fried in Olestra have 75 calories (instead of the 150 calories corresponding to chips fried in fat the traditional way). Like fat, Olestra is nonpolar and can dissolve other fat-soluble substances, including the fat-soluble vitamins A, D, E, and K. It is problematic that Olestra absorbs these vitamins that are stored in fat and are necessary for good health. Olestra is therefore fortified with vitamins A, D, E, and K to prevent it from depleting the body's supply of these vitamins. Although the U.S. Food and Drug Administration has found Olestra to be safe and has approved its use in snack foods, it required warnings on products containing Olestra because of undesirable side effects, such as diarrhea and abdominal cramping.

A third fat substitute, Z-Trim, has been developed by the U.S. Department of Agriculture. Originally called Oat-Trim, it is made from agricultural by-products, such as the hulls of oats, peas, soybeans, and rice, or bran from corn or wheat. Because it is made from natural dietary fibers, it is digestible. Not only does it lower fat consumption, it also provides fiber for the diet. Z-Trim can be used as a fat substitute in cheese products, baked goods, and hamburgers. Brownies containing Z-Trim are 16 percent fat (compared to 25 percent for traditional brownies).

Although fat substitutes may reduce the caloric contents of the foods in which they are used, caution is still necessary. Foods labeled "fat free" are not "calorie free." If an individual feels that he or she can eat more of a food containing a fat substitute, his or her total caloric intake may actually increase. SEE ALSO DETERGENTS; LIPIDS; SOAP.

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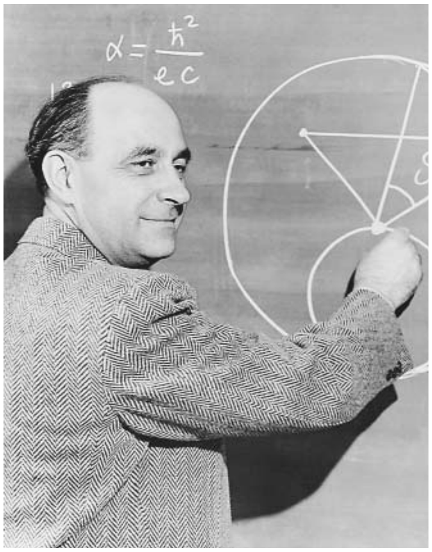
Fermi, Enrico

AMERICAN PHYSICIST
1901–1954

Enrico Fermi was born in Rome, the son of Italy's chief railroad inspector (Alberto Fermi) and a schoolteacher (Ida de Gattis). While he was attending Ginnasio Liceo Umberto I, an associate of his father recognized Fermi's talents in physics and mathematics and encouraged him to master several challenging scientific treatises. At the University of Pisa and the Scuola (1918–1922), Fermi published two papers on relativistic electrodynamics and one on general relativity. He completed doctoral theses at each institution. After holding several short-term positions, Fermi attracted the attention of Italian senator and chemist Orso M. Corbino, who helped establish for Fermi the country's first chair of **theoretical physics** at the University of

theoretical physics: branch of physics dealing with the theories and concepts of matter, especially at the atomic and subatomic levels

Rome. In 1928 Fermi married Laura Capon, and the couple had two children.



American physicist Enrico Fermi, recipient of the 1938 Nobel Prize in physics, "for his demonstrations of the existence of new radioactive elements produced by neutron irradiation, and for his related discovery of nuclear reactions brought about by slow neutrons."

α-particle: subatomic particle with 2+ charge and mass of 4; a He nucleus

nuclear: having to do with the nucleus of an atom

Manhattan Project: government project dedicated to creation of an atomic weapon; directed by General Leslie Groves

fissionable: of or pertaining to unstable nuclei that decay to produce smaller nuclei

As a chair at the University of Rome, Fermi did much of his most important work between 1927 and 1938. Along with the English physicist Paul Dirac but independently, he developed quantum-mechanical statistics that measure particles of half-integer spin (now known as fermions); between 1929 and 1932 he reformulated more simply and elegantly Dirac's then recent work on quantum electronics. In 1933–1934, he published a theory of β-decay that included what became known as the Fermi interaction, Fermi interactions, and the Fermi coupling constant. He also theorized and named the neutrino ("little neutral one"), originally hypothesized by Wolfgang Pauli but not detected experimentally until 1956.

After 1933 Fermi turned increasingly to experimental physics. Inspired by recent work in which artificial radioactive substances were produced by **α-particle** bombardment, Fermi and several collaborators used neutron bombardment to create several "transuranic" elements heavier than uranium, including plutonium. This work, and his finding that slow neutrons produce **nuclear** reactions more efficiently than fast ones, earned Fermi wide acclaim and the 1938 Nobel Prize in physics. After accepting the prize in Sweden, Fermi and his Jewish wife immigrated to the United States to escape the Nazis.

After replicating the German fusion of the uranium atom in early 1939, Fermi was recruited to join the secret U.S. atomic bomb project, the **Manhattan Project**. He initially worked at the project's metallurgical laboratory at the University of Chicago, where he was chief designer of an atomic pile that achieved a sustained nuclear reaction on December 2, 1942. Throughout the war he worked on reactor design and **fissionable** fuel production at several project facilities.

Fermi became a naturalized U.S. citizen on July 11, 1944. Short in stature and barrel-like, he retained a thick Italian accent and refreshingly unassuming manner throughout his life. Although he supported the atomic bombing of Japan, after the war, as a member of the powerful General Advisory Committee of the Atomic Energy Commission, he opposed the development of a hydrogen bomb. Fermi moved into new areas of research, including cosmic rays (the "Fermi mechanism" modeled their acceleration) and elementary particle physics. In addition to the Nobel Prize, Fermi was honored with many other distinguished awards, including the Presidential Medal of Merit (1946), the Franklin Medal (1947), the Max Planck Medal (1954), and the Fermi Award (1954). The latter, as well as the Fermi National Accelerator Laboratory in Batavia, Illinois, were named in his honor. SEE ALSO NUCLEAR CHEMISTRY; PAULI, WOLFGANG.

David B. Sicilia

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Fermium

MELTING POINT: **1800K**
BOILING POINT: **unknown**
DENSITY: **unknown**
MOST COMMON IONS: **Fm^{3+}, Fm^{2+}**

100
Fm
FERMIUM
257

Fermium, the eleventh member of the actinide series, was discovered in 1952. Fermium (element 100), together with einsteinium (element 99), were unexpectedly produced in the explosion of the first U.S. thermonuclear device, "Mike," tested at Eniwetok Atoll in the South Pacific on November 1, 1952. Fermium was first identified in the form of the ^{255}Fm (half-life 20 hours). The name fermium was chosen for element 100, in honor of the great physicist Enrico Fermi. Fermium **isotopes** of masses 242 through 260 are known. All are radioactive, decaying via **α-particle** emission, electron capture, and spontaneous **fission**. The isotope of mass 258 has the shortest half-life (0.4 milliseconds), and that of mass 257 has the longest (100.5 days). It is noteworthy that a predominantly symmetric mass division (during spontaneous fission) was first observed in ^{259}Fm. The ground state electronic configuration of the gaseous fermium atom is $[Rn]5f^{12}7s^2$, analogous to that of its **lanthanide** homologue (erbium). The most stable ion in **aqueous solution** is Fm^{3+}, although Fm^{2+} and Fm^{4+} have been reported. However, the claim of the identification of the latter two ions has not been substantiated. As with einsteinium, divalency is seen in the **metal**. SEE ALSO Actinium; Berkelium; Einsteinium; Fermi, Enrico; Lawrencium; Mendelevium; Neptunium; Nobelium; Plutonium; Protactinium; Radioactivity; Rutherfordium; Thorium; Transactinides; Transmutation; Uranium.

Darleane C. Hoffman

isotope: form of an atom that differs by the number of neutrons in the nucleus

α-particle: subatomic particle with 2+ charge and mass of 4; a He nucleus

fission: process of splitting an atom into smaller pieces

lanthanides: a family of elements from lanthanum to lutetium having from 1 to 14 4f electrons

aqueous solution: homogenous mixture in which water is the solvent (primary component)

metal: element or other substance the solid phase of which is characterized by high thermal and electrical conductivities

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Fertilizer

A fertilizer is a plant nutrient added to a soil to increase its yield. Plants need nutrients to grow and produce fruits and vegetables. Two categories of nutrients have been identified in fertilization: **macronutrients** and micronutrients. There are only six macronutrients and they are required in large amounts by plants: nitrogen, phosphorus, potassium, sulfur, magnesium, and calcium. However, a larger number of micronutrients are required but in trace amounts: iron, manganese, boron, zinc, copper, molybdenum, chlorine, cobalt, nickel, sodium, and silicon. Eliminate any of these elements, and plants will display abnormal growth and deficiency, or they may not reproduce.

macronutrient: one of a number of substances, needed in relatively large amounts, that provide nourishment for living organisms

The most popular fertilizers contain the three major nutrients: nitrogen, phosphorus, and potassium, and they are therefore referred to as NPK fertilizers. To illustrate their importance in any economy, in 2000, the world consumption of the total fertilizer nutrient ($N + P_2O_5 + K_2O$) was 140

Fertilizer is being applied in a rice field.

million tons, representing 52 million tons for developed countries and 88 million tons for developing countries.

chlorophyll: active molecules in plants undergoing photosynthesis

vitamins: organic molecules needed in small amounts for the normal function of the body; often used as part of an enzyme catalyzed reaction

Nitrogen forms part of proteins, hormones, **chlorophyll**, **vitamins**, and enzymes, and promotes stem and leaf growth. Too much nitrogen can delay fruiting, while a deficiency of it can reduce yields and induce yellowing of leaves and stunted growth. Nitrogen fertilizers are applied in organic and/or inorganic forms. Organic nitrogen fertilizers are farmyard manure, guano (excreta and remains of seabirds), dried blood, hoof, and horn. However, organic nitrogen sources must undergo microbial processes that produce nitrate nitrogen.

cyanobacterium: eubacterium sometimes called "the blue-green alga"; it contains chlorophyll (the pigment most abundant in plants), has very strong cell walls, and is capable of photosynthesis

Inorganic nitrogen sources are directly available to plants and include the following: sodium nitrate, calcium nitrate, ammonium sulfate, ammonium nitrate, urea, calcium cyanamide, and ammonia. In addition, atmospheric nitrogen may be used as a source of plant nitrogen by the process called "nitrogen fixation." Legumes and a few other plants, in association with **cyanobacteria** (microscopic aquatic bacteria, for example, *Anabaena azollae*), convert nitrogen to biologically useful ammonia. This process occurs in small growths on the roots called "nodules." Ammonia is subsequently available for many biological molecules, such as amino acids, proteins, vitamins, and nucleic acids.

seed germination: beginning of the process by which a seed produces a new plant

photosynthesis: process by which plants convert carbon dioxide and water to glucose

Phosphorus plays an important role in **seed germination**, **photosynthesis**, protein formation, overall growth and **metabolism**, and flower and fruit formation. Phosphorus deficiency induces purple stems and leaves, poor flowering and fruiting. Low soil pH (<4) ties up phosphates by favoring the formation of insoluble aluminum and iron phosphates. Phosphorus fertilizers come from different sources: bones, rock phosphate, superphosphate (a mixture of calcium dihydrogen phosphate and calcium sulfate), nitrophosphate, ammonium phosphate, basic slag (by-product in steel manufacture), etc.

metabolism: the complete range of biochemical processes that take place within living organisms; comprises processes that produce complex substances from simpler components, with a consequent use of energy (anabolism), and those that break down complex food molecules, thus liberating energy (catabolism)

Potassium contributes to the formation of sugars, carbohydrates, proteins and to cell division; adjusts water balance; enhances the flavor, color, and oil content of fruits; and is very important for leafy crops. Potassium deficiency produces a spotted, curled, or burned appearance to leaves and lowers crop yields. Potassium fertilizers are applied in the following forms: potassium chloride, potassium sulfate, potassium nitrate, and wood ash.

Other macronutrients are supplied as part of NPK fertilizers. First, sulfur is available from the sulfate of fertilizers. It contributes to the formation of amino acids, proteins, and enzymes, and is essential to chlorophyll. It also affects flavor in many vegetables. Second, magnesium is naturally present in the soil and is generally associated with potassium sulfate and calcium phosphate, used as NPK. It is a critical part of chlorophyll, and contributes to the functioning of enzymes for carbohydrates, fruit and nut formation, and the germination of seeds. Magnesium deficiency induces yellowing between the veins of older leaves, and leaves droop (hang down) as a result. Finally, calcium is also present in the soil and is available from calcium phosphate and nitrate, and lime. It activates enzymes, contributes to the structural part of cell walls, and influences water movement, cell growth, and division.

Micronutrients are not specifically applied to soil since they are naturally found in soils. However, there are some extreme cases where they must be supplied. For example, animal disorders have been linked to a lack of trace amounts of elements, not necessary for plant growth but essential for some species of animals. In some parts of Great Britain, for example, sheep and cattle suffered from "pining disease" that resulted in severe weight loss and general debilitation. The disease was found to result from a shortage of cobalt in the herbage. It has also been established that selenium deficiencies in some soils cause **muscular dystrophy**, while selenium excesses induce **selenium toxicity** in livestock. SEE ALSO CALCIUM; CARBOHYDRATES; ENZYMES; MAGNESIUM; NITROGEN; NUCLEIC ACIDS; PHOSPHORUS; POTASSIUM; PROTEINS; SILICON; SULFUR.

muscular dystrophy: medical condition in which there is gradual atrophy of skeletal muscles

selenium toxicity: condition created by intake of excess Se from plants or seleniferous water; acute and chronic toxicity are known

Joseph Bariyanga

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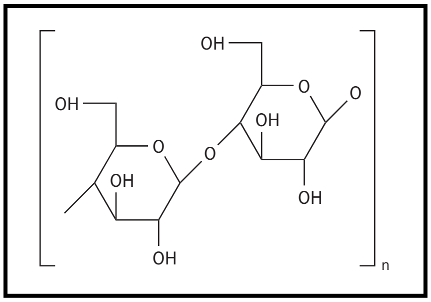
Fibers

Fibers are long strands of molecules interwoven to form a linear, stringlike structure. They may be natural or made by humans and are essential to



A portion of a cellulose fiber.

clothing, industry, and our very bodies. Natural fibers are of plant or animal origin. In many cases, synthetic fibers mimic natural fibers.

Natural Fibers

Among the natural fibers are cellulose, the primary structural component of plants and bacterial cell walls; animal fibers such as wool and silk; and biochemical fibers. Plant fibers are composed of cellulose (see Figure 1), lignin (see Figure 2), or similar compounds; animal fibers are composed of protein (see Figure 3).

Cellulose, the most widespread organic molecule on Earth, is the major component of plant cell walls. Plants produce approximately 50 kilograms of cellulose daily for each person on Earth. A linear polymer made up of 10,000 to 15,000 glucose molecules bonded in a 1 → 4 glycosidic linkage, it is made up almost entirely of glucose. Cellulose molecules contain many polar hydroxyl groups, which allow them to interact with adjacent molecules to form fibers. These fibers are structurally strong and resistant to chemical attack, so wood products are widely used in construction and production of paper.

Cotton, a vegetable fiber that is almost pure cellulose, grew to become an important industrial commodity during the nineteenth century. Composed of cellulose strands in small springlike coils, cotton fibers have no surface scales and are softer than wool and less likely to provoke itching. First used as a textile material in India, cotton is now grown in every temperate part of the world and has been an important commodity in the southern United States. Cotton plants grow seed cases called bolls that yield tangled masses of fibers which are easily collected and spun. Processing cotton fibers is done in much the same way as wool.

Natural fibers such as cotton can be chemically modified to form rayon or acetate. Rayon was first called artificial silk. In the viscose process, cellulose is dissolved in sodium hydroxide, pushed through spinnerets, and treated with acid to harden. Treatment with copper compounds and ammonia is used to form hosiery yarns. Acetate (or cellulose acetate), produced by treating cotton with acetic acid and acetic anhydride, is also used in production of clothing.

Hemicellulose is similar in structure to cellulose, but chains of hemicellulose are shorter and less stable. Soluble hemicellulose chains attract water and form gels. Unlike cellulose, hemicellulose is a polymer of various monosaccharides, such as glucose, galactose, mannose, xylose, and arabinose.

polymer: molecule composed of many similar parts

Lignin **polymers** are often found in most plant structures in association with cellulose. The structure of lignin is not well defined, but lignin appears to be made up of polymers of propylbenzene with hydroxy and methoxy groups attached. Lignin is primarily hydrocarbon in nature and makes up a major portion of insoluble dietary fiber.

Animal Fibers. Animal hair composed of protein is a common biological fiber. Numerous types of hair have been used commercially for weaving, production of ropes, padding, and insulation.

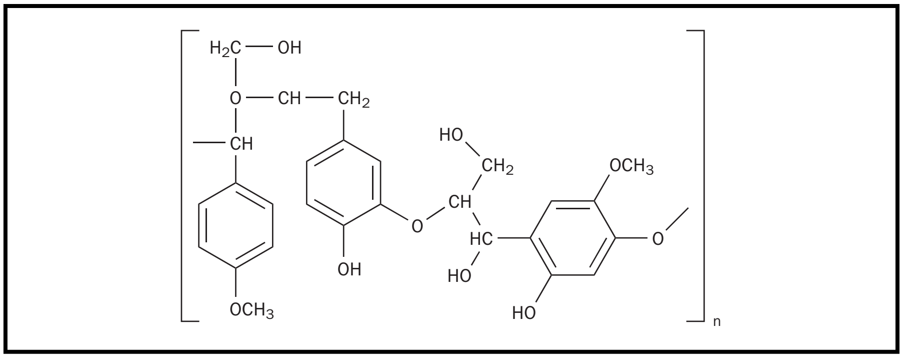


Figure 2. A portion of one of the many possible structures of lignin.

Wool fibers are made of animal hair, principally from sheep. Each hair is a complex structure made up of layers of protein molecules. Cloth made from wool has excellent insulating properties and resists wrinkling. Wool fibers can be stretched, dyed, and woven.

For centuries, sheep have been bred for their wool-bearing qualities. Production of woolen fabrics is a highly technical process. In its simplest form, sheep are sheared and the wool sorted and cleaned, then the wool is carded to straighten the fibers, spun into thin cords, and woven into fabrics. Each step in this process has been refined to provide a high-quality product of vast commercial importance.

Silk is an animal fiber valued for its texture, strength, and luster. First prepared in ancient China, silk fabric was expensive, luxurious, and soft; its popularity led to the development of a trade route known as the Silk Road leading from Asia to Europe. Early American entrepreneurs such as Benjamin Franklin promoted the silk industry in the colonies. Silkworms spin cocoons that are collected, steamed, and unwound to obtain the silk fiber by a process known as reeling. A number of fibers are twisted together to form a thread of raw silk. Threads are combined, cleaned, stretched, dyed, and woven into fine fabrics. Silk fibers have great tensile strength and are sometimes used in **cordage**.

cordage: rope or twine created by twisting individual fibers into strands and twisting strands into cords

Polymers of amino acids held together by amide linkages form the primary structures of proteins. In the portion of a protein molecule shown in figure 3, the amino acids glycine, cysteine, valine, and serine are joined by amide (peptide) bonds to form a tetrapeptide segment. In addition to hair and silk, proteins are found in some important cellular substances. Some fibers are single molecules; others are combinations of molecules lying side by side and covalently cross-linked or held in place by hydrogen bonds. Collagen fibers found in tendon, bone, and skin are side-by-side assemblies of tropocollagen. Each tropocollagen molecule consists of three polypeptide chains wound into a triple helix. Separation of collagen fibers by boiling produces gelatin. Bacterial flagella, the fibrin that helps to form blood clots, and muscle fibers also fall under the heading of fibers.

In the fine structure of cells, microtubules make up fibers such as the spindle fibers that attach to centromeres of chromosomes to pull chromatids apart during mitosis and meiosis. Microtubules function in a number of cellular processes, including motility of cells and subcellular components. Microtubules assemble into tubulin, a substance that can change the shape of cells.

A carpet trader in Sarajevo, Bosnia and Herzegovina. Wool fibers are refined to produce high-quality fabrics for numerous commercial purposes.

Actin and myosin fibers or filaments make possible the contraction of muscles. Actin and myosin fibers in muscle lie side by side and react chemically, sliding together and apart to shorten and lengthen in response to energy from adenosine triphosphate.

Inorganic Materials. A few inorganic materials form fibers. Fiberglass made of spun glass has excellent insulating properties. Mixed with epoxy resins, fiberglass is an important reinforcing component for use in such products as automobile bodies and boats. Steel fibers can be pressed into steel wool pads, widely used for their abrasive quality, or they can be braided or twisted into ropes.

Carbon can be treated at high temperature to form strong, light fibers that are mixed with other materials such as epoxy resin to form composites similar to those reinforced with fiberglass but lighter and stronger. Most

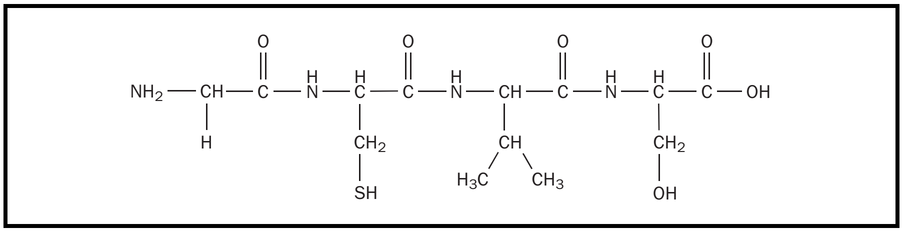


Figure 3. Glycylcysteinylvalylserine, a tetrapeptide portion of a protein molecule.

carbon fiber technology converts the carbon to graphite, which forms long, thin ribbons that pack together to form fibers. Carbon fibers show promise as components of composites for aircraft and autos, but the added expense has limited carbon fiber technology to production of high-quality devices such as golf clubs, fishing rods, bicycles, tennis rackets, and luxury autos. A new technique allows the formation of remarkably strong and light carbon nanofibers. These nanofibers show promise as bases for catalysts and as microconductors that may form important components of future computers.

Asbestos fibers occurring naturally in minerals such as serpentine were once valued for their insulating qualities and resistance to chemical attack. Locomotive and industrial boilers, pipes, and cargo compartments of ships were once coated with asbestos. However, there have been so many cases of workers in the asbestos industry developing respiratory illnesses such as asbestosis or mesothelioma that asbestos is no longer being used and in many places it is being removed.

Both gold and silver can be made into threads, which can be used as electrical conductors or in production of decorative fabrics. Many valuable examples of gold tapestries, carpets, or canopies for thrones exist. The durability and luster of gold undoubtedly contribute to its value.

Synthetic Fibers

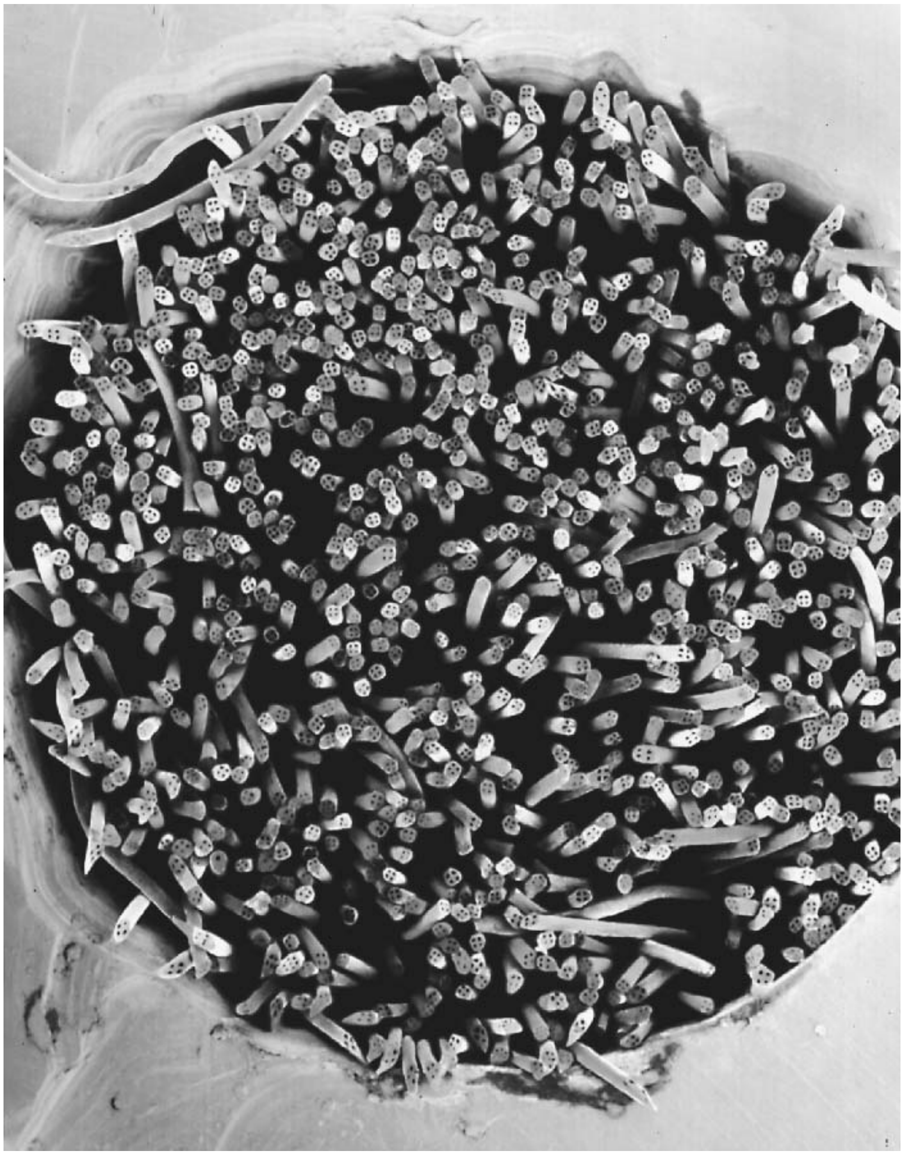
Synthetic fibers are usually polyesters or polyamides. The most important synthetic fibers are dacron, nylon, orlon, and polypropylene (primarily used for upholstery).

Acrylic fibers are vinyl polymers valued for resistance to chemical and biological degradation. Acrylonitrile (or vinyl cyanide) forms a homopolymer that is used in filters and artificial wool, which is widely used in sweaters.

Condensation fibers such as nylon and polyethylene terephthalate are formed when two or more different monomers react, releasing small molecules such as water, and forming amide or ester bonds between the monomers. Nylon, first produced by DuPont in 1938, became a mainstay of the hosiery industry and is now the most widely used fiber in carpet manufacture. Polyethylene terephthalate, produced by formation of an **ester** bond between terephthalic acid and ethylene glycol, is by far the most widely used synthetic fiber.

ester: organic species containing a carbon atom attached to three moieties: an O via a double bond, an O attached to another carbon atom or chain, and an H atom or C chain; the R(C=O)OR functional group

Teflon, discovered accidentally by Roy Plunkett at DuPont, is formed by polymerizing tetrafluoroethene. Teflon has a low coefficient of friction and is remarkably resistant to chemical attack. The ability of Teflon to flow under pressure makes it an ideal sealant for pipe threads and vessels, and



A microscopic view of dacron polyester fibers.

its low coefficient of friction makes it valuable as a component of self-lubricating bearings. The molecular weight of Teflon is high, but Teflon powders can be formed into many shapes, including artificial joints for use in the human body and fibers used in clothing.

Kevlar, a polymer of aromatic amides, is several times stronger than steel, but much lighter and also fire resistant. Kevlar fibers are formed into hollow cylinders that are then woven into fabrics useful in bullet-proof vests and manufacture of automobile tires. SEE ALSO CELLULOSE; POLYESTERS; POLYMERS, SYNTHETIC.

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Fibrous Protein

Many of the familiar cells in your body use fibrous proteins to carry out important tasks. Skin, bones, muscles, tendons, and hair cells all rely on molecules in this class.

The amino acid sequences of fibrous proteins often contain repeating sets of **amino acid residues**. Such repeating sets tend to cause the protein to be both elongated and strong.

amino acid residue: in a protien, which is a polymer composed of many amino acids, that portion of the amino acid that remains to become part of the portein

Human hair provides a good example of how fibrous proteins have structural functions. The main protein in hair is called alpha-keratin. More than twenty-five variations of alpha-keratin are found in the cells of mammals. Individual molecules of alpha-keratin are not particularly large, but they provide the structure for hair by forming a coil of coils. Clustering several smaller structures to make a larger filament adds strength in the same way that strong ropes are made from groups of smaller twine.

Fibrous proteins also gain strength due to interactions between the side chains of the residues. The alpha-keratin **polypeptides**, for example, have a large number of cystine residues, which can form **disulfide bonds**.

polypeptide: compound containing two or more amide units—C(O)NH—produced by the condensation of two or more amino acids

disulfide bond: two bonding sulfur atoms, –S–S–

When a person gets a “permanent,” the first chemicals that are applied break the disulfide bonds. The hair is then curled (or straightened), and

A scanning electron micrograph of eyelashes growing from the surface of human skin.

another chemical is applied to reform the disulfide bonds so the new style is retained permanently.

Coils such as those found in alpha-keratin are not the only structural motifs present in fibrous proteins. Silk, for example, is largely composed of fibrous proteins whose structures resemble interleaved sheets. SEE ALSO Quaternary Structure; Secondary Structure; Tertiary Structure.

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Fire, Fuels, Power Plants

Fire is a phenomenon of combustion, usually the reaction of a substance with oxygen, producing heat, light, and gases. It has been used for entertainment, religious ceremonies, destruction, and energy. Typical fires involve wood, paper, or hydrocarbon fuels combining with oxygen in air, but many substances such as metals burn in atmospheres of chlorine or fluorine.

Fire, considered by ancient Greeks to be one of the four elements, has been worshiped and is often invoked in religious ceremonies. Fires provide a source of energy as well as adding to the entertainment of an evening at home or around a campfire.

The fire from candles has provided light for centuries. Capillary action carries melted wax along the wick from the candle to the flame. As the wax burns, it produces a characteristic teardrop-shaped flame as air is heated and expands, moving upward. In the microgravity of space, candle flames slightly influenced by gravity are round or dome-shaped.

oxidation: process involving the loss of electrons (or the addition of an oxygen atom)

Oxidation is a chemical process in which the substance being oxidized loses electrons to another substance that is simultaneously reduced. Magnesium metal burns vigorously in air, producing flames and magnesium oxide. The flames produced in this reaction are caused by heating magnesium oxide particles until they incandesce, radiating visible light. Similarly, when a hydrocarbon fuel burns, particles of carbon incandesce, emitting light and passing into the surrounding air as smoke.

Efficient and complete combustion of a hydrocarbon such as methane yields carbon dioxide and water:

$$CH_4 + 2\ O_2 \rightarrow CO_2 + 2\ H_2O + \text{heat}$$

Incomplete combustion caused by insufficient oxygen yields water and carbon monoxide or carbon in place of carbon dioxide. Small amounts of carbon monoxide in air are probably harmless, but carbon particles form soot, which often contains dangerous polycyclic hydrocarbons and may carry dangerous gases into the alveoli of lungs. Carbon monoxide is a colorless, odorless, poisonous gas. Furnaces are designed to burn natural gas with a blue flame, indicating production of little carbon, and probably little carbon monoxide.

Power Plants

Fire also provides energy for power plants. Energy is defined as the ability to do work, power is defined as the rate of doing work. An incandescent light bulb is rated in terms of power. A 100-watt bulb uses power at the rate of 100 watts. Power is commonly measured in watts or joules. One watt is equivalent to 1 joule per second, so a 100-watt incandescent bulb would use 100 joules of energy per second. Burning the electrical bulb for ten hours uses 1 kilowatt-hour of energy at the rate of 100 watts per hour. Homeowners purchase electrical energy, not power.

Power plants typically consist of a generator to produce electricity and a power source to operate the generator. The source of energy may be nuclear reactions or fossil fuels such as natural gas, oil, or coal. The fuel may be burned to boil water, producing steam, or burned in a diesel or internal combustion engine to turn the generator. Most thermal power plants burn fuel to boil water, forming steam, then pass the steam through turbines that spin generators, producing electricity.

The location of power plants is determined in part by the need for electricity, the availability of fuel, and water for cooling. The Four Corners power plant located at the junction of Colorado, New Mexico, Arizona, and Utah is one of the largest plants in the United States. It burns 28,000 tons of coal per day and produces 2,040,000,000 watts of power. Located far from urban areas, the plant's emissions originally seemed to pose less danger to humans than urban plants, but environmental concerns soon demanded more stringent emission controls. Emissions from the plant, located in a rural area, are now more carefully controlled, fuel from nearby coal mines is readily available, and cooling water from nearby rivers makes the energy-generation process more efficient.

Electrical energy is fed into power transmission grids that span several states. A number of power plants produce electricity that goes into the grids and is used by consumers many miles away. Distribution of alternating current allows the voltage to be stepped up by passage through transformers prior to distribution. High-voltage electricity can be transmitted more efficiently than low voltages, and the voltage is reduced through step-down transformers and transferred to distribution grids before use by consumers.

Nuclear power plants use **fissionable** materials such as uranium-235 as sources of energy. In the core of a nuclear power plant, rods of uranium dioxide (UO_2) are placed in a matrix containing moderators such as heavy water or graphite that slow neutrons so they can be captured. The neutrons impact uranium nuclei, splitting them to release lighter nuclei and converting a small amount of mass to energy. In order for a chain reaction to occur, a critical mass of fissionable material must be present.

fissionable: of or pertaining to unstable nuclei that decay to produce smaller nuclei

Nuclear power plants are designed to prevent accidents such as meltdown by careful control of fuel-rod placement and positioning of control rods made of boron or other materials that have high affinity for neutrons. If the core of the reactor should become overheated, the fuel rods are automatically pulled out of the reactor and the control rods drop in, cutting the supply of neutrons. In addition, the core of the reactor is positioned over a number of separate wells into which components would fall, separating the fissionable materials to less than a critical mass.

fusion: the act of releasing nuclear energy by combining lighter elements such as hydrogen into heavier elements

Fusion promises to provide a nearly inexhaustible supply of hydrogen fuel as well as less radioactive waste, but temperatures of fusion reactions are too high for present materials, and the huge amounts of energy needed to start fusion reactions would explode or melt any known construction materials. The fires of nuclear fusion in our Sun provided energy for early humans long before they discovered the art of combustion. SEE ALSO CHEMICAL REACTIONS; CHEMISTRY AND ENERGY; EXPLOSIONS; FOSSIL FUELS.

Dan M. Sullivan

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Fireworks

One of the most beautiful and entertaining uses of fire occurs in firework displays. Fireworks need a source of combustible material for energy such as black powder, a mixture of charcoal, sulfur, and saltpeter (an old name for potassium nitrate), or smokeless powder such as cellulose nitrate. In addition, fireworks contain substances that give off bright, colorful light when heated. A common example of such material is sodium in table salt. If salt is sprinkled into a flame, an orange color appears. The colored flame is a result of electrons in sodium ions absorbing energy and moving up to higher energy levels and then falling back to their ground state, emitting specific amounts of energy that correspond to colors of light. For centuries, this phenomenon has been the basis of flame tests in chemistry laboratories.

Chemical ingredients of fireworks are chosen to produce specific colors. Barium compounds produce green colors when heated, copper salts produce green and blue flames, sodium salts are yellow in flame, lithium compounds produce red colors, magnesium metal produces brilliant white light when burned, and strontium compounds produce brilliant red colors. Salts used contain both metallic cations and nonmetallic **anions**. Anions such as chlorates, perchlorates, and nitrates also contribute **oxidizing** power to the chemical mixture.

anions: negatively charged chemical unit, such as Cl^-, CO_3^{2-}, NO_3^-

oxidation: process involving the loss of electrons (or the addition of an oxygen atom)

Chemical Element	Color Produced
sodium	yellow
barium	green
strontium	red
copper	blue

While the metallic element dictates the color produced, the compound that contains the element has a profound effect on the type of flame. Calcium does not produce an exciting color by itself, but it enhances colors of other substances. Chlorine does not produce colored flames by itself, but the presence of chlorine greatly enhances the development of color from metallic elements. Chlorine-containing substances such as chlorate or perchlorate oxidizers or organic chlorine compounds such as polyvinyl chloride or hexachlorobenzene provide chlorine atoms to enhance volatility and light emission. Certain substances are included for specific effects. Iron filings sparkle and flash when mixed with other burning materials; the metallic iron oxidizes to produce Fe_2O_3, a process that produces a large amount of energy sufficient to cause the reacting iron particles to glow. Titanium metal is also used for production of sparks. Zinc is used in some smoke formulas and to produce star effects.

Fireworks consist of a source of energy such as a mixture of a fuel and an oxidizing agent that react to produce high temperatures and some substance that will emit brightly colored light. One of the simplest firework devices is a sparkler. Sparklers typically consist of a metal wire coated with a mixture of fuel and an oxidizer (mixed in proportions to allow burning), iron filings, and a glue to hold the components together. When the sparkler is ignited, the fuel and oxidizer burn, heating the iron filings so that they sparkle. Other substances such as zinc or magnesium alter the character of the sparks.

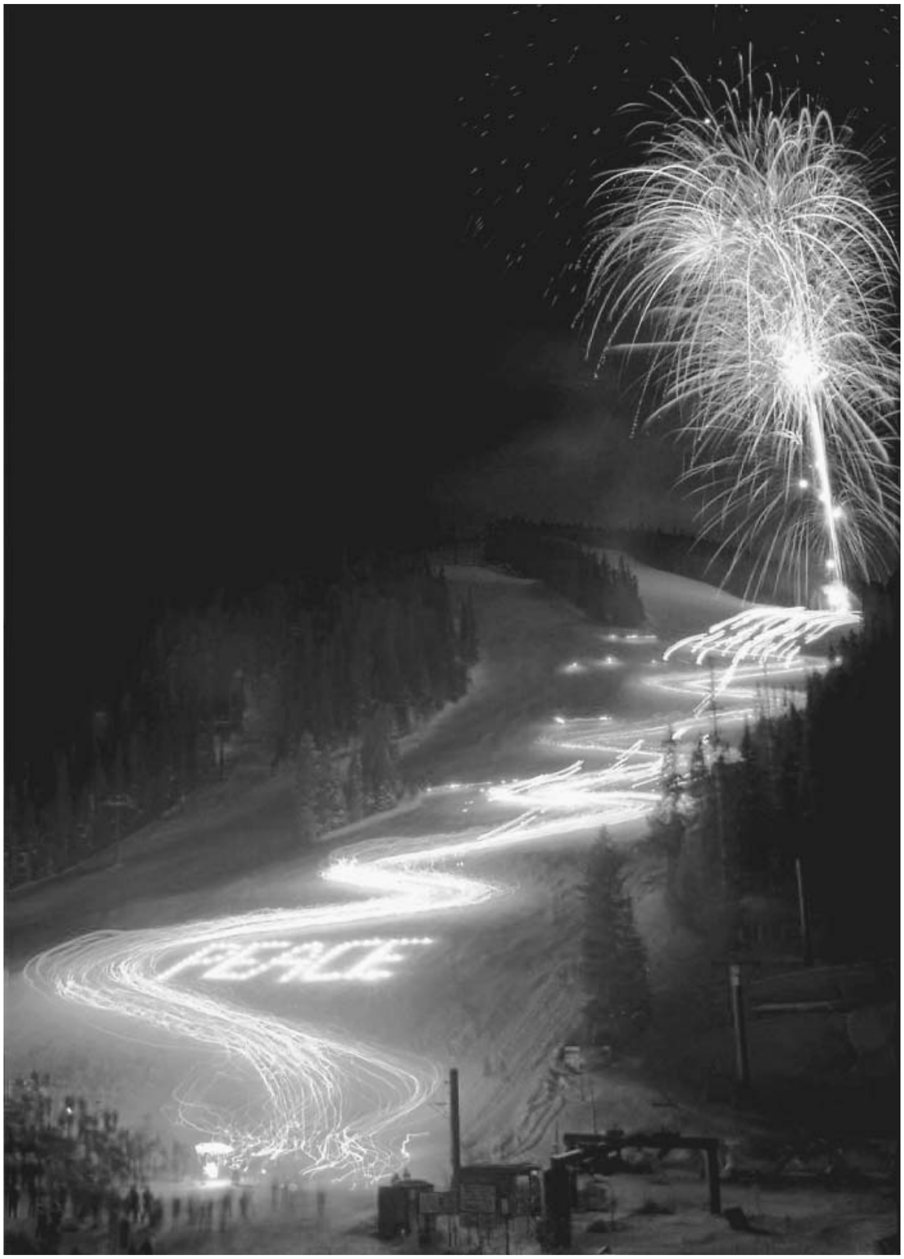
Firecrackers contain flash powder (a mixture of an oxidizer such as potassium chlorate or perchlorate and powdered aluminum or magnesium) or black gunpowder in a paper tube. An attached fuse ignites the flammable mixture, which burns explosively, producing gases that rapidly build up pressure and burst the container. Aluminum and magnesium components produce brighter flashes.

Aerial fireworks usually are of two types, aerial shells fired from tubes and the traditional skyrocket. Rockets are made of cardboard tubes filled with a mixture of fuel and oxidizer in proportions that allow continuous burning rather than explosion. Expulsion of gases from the tube propels it skyward. Rockets often contain explosive charges to explode after the propellant charge burns out; the composition of the explosive charge determines the colors produced.

Aerial shells are small balls of explosive material fired from a steel or cardboard tube or stand. A lifting charge throws the ball skyward, and the explosive charge fires when the embedded fuse burns down after a time period appropriate for the shell to reach the desired altitude. The shell usually contains a bursting charge and stars made up of cubes or spheres of material that will burn, sparkle, or explode. Multibreak shells are made up of combinations of shells designed so that the explosion of one shell ignites the next.

Shells designed to explode with a bang are called reports or salutes. The whistling effect of some devices is produced by packing techniques that cause intermittent burning. Specialized shells designed to burst forming patterns such as hearts or circles are made by surrounding the break charge with pellets containing explosive charges. When the break charge explodes, the pellets are blown outward, producing a pattern.

In addition to their value as entertainment, pyrotechnics have military applications as signaling, training, and combat devices. Burning naphthalene and anthracene produce black smoke that can be used to screen off an



Torchlight parade of skiers, Winter Park, Colorado, December 24, 1995.

area, but may be dangerous in populated areas. White smoke produced by vaporizing zinc chloride or oil or burning phosphorus is sometimes used to provide cover during combat; the hydrolysis of silicon chloride ($SiCl_4$) produces a white smoke as well.

$$SiCl_4 + H_2O \rightarrow SiO + HCl$$

The moisture in the air is usually sufficient for producing the desired reaction. Colored smokes for signaling are usually produced by volatilization of organic dyes. Burning mixtures that provide enough heat to vaporize the dye, but not enough to decompose it, are chosen. Dyes chosen must be volatile, but nontoxic.

A simple and safe home experiment can be carried out by squeezing an orange peel near a candle flame. The oils of the peel produce tiny flashes of light as they burn. Bananas contain large amounts of potassium; a banana peel in a bonfire shows the characteristic violet color of potassium flames. SEE ALSO Chemistry and Energy; Explosions.

Dan M. Sullivan

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Fischer, Emil Hermann

GERMAN CHEMIST
1852–1919

Emil Hermann Fischer, born October 9, 1852, in Euskirchen, Germany, received the Nobel Prize in chemistry in 1902 for his elucidations of the structure of sugars and the **synthesis** of purines. His father, a very successful lumber merchant, intended Emil to join the family business upon completion of his secondary school education. Young Fischer showed exceptional abilities as a student in the natural sciences, particularly in physics. In 1859 he dutifully entered his father's business, but showed little aptitude for commerce. In frustration his father enrolled him at the University of Bonn in 1871 to study chemistry, which at least had practical applications.

synthesis: combination of starting materials to form a desired product

The following year he transferred to the University of Strasbourg, where he attended the lectures of Adolf von Baeyer. He gave up any remaining interest in physics for a career in organic chemistry. Fischer pursued graduate studies in chemistry under von Baeyer's mentorship, and was awarded a doctorate degree in 1874. In the course of his doctoral research he synthesized the compound phenylhydrazine, which would prove to be invaluable in his studies of carbohydrates (but would also, because of his prolonged exposure to it, leave him with cancer).

In 1875 Fischer followed von Baeyer to the University of Munich, and in 1881 he obtained his first academic post as professor of organic chemistry at the University of Erlangen. This was followed by his being called to the University of Würzburg in 1888, and finally, in 1892, to the University of Berlin, where he remained until his death in 1919. His son Hermann Otto (1888–1960) went on to have a distinguished career in biochemistry.

Fischer's most important scientific work was carried out between 1882 and 1906. Little was known about the naturally occurring sugars when Fischer began his investigations of them in 1884. Four sugars were known at that time: **glucose**, **galactose**, fructose, and sorbose, each having the formula $C_6H_{12}O_6$. It was known that each had a six-carbon chain, and five alcohol groups as well as a carbonyl (**aldehyde** or **ketone**) **functional group** attached to the chain.

glucose: common hexose monosaccharide; monomer of starch and cellulose; also called grape sugar, blood sugar, or dextrose

galactose: six-carbon sugar

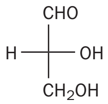
aldehyde: one of the characteristic groups of atoms in organic compounds that undergoes characteristic reactions, generally irrespective of where it occurs in the molecule; the RC(O)H functional group

ketone: one of the characteristic groups of atoms in organic compounds that undergoes characteristic reactions, generally irrespective of where it occurs in the molecule; the FC(O)R functional group

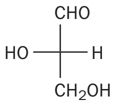
functional group: portion of a compound with characteristic atoms acting as a group

Fischer saw in the sugars what no one else had seen. In 1874 Dutch chemist Jacobus van't Hoff had proposed that molecules in which a central carbon atom is bonded to four constituent atoms had a tetrahedral geometry in space, and that if a carbon atom were bonded to four different constituents, the molecule could exist in two forms (as stereoisomers) that were mirror images of one another. These two forms would possess distinct right- and left-handedness. Fischer realized that in glucose there were four carbon atoms that met the criteria for exhibiting stereoisomerism. A glucose molecule would exist as one of sixteen possible stereoisomers, each differing only by its orientation in space. Using the methods of chemical synthesis and degradation that were available to him, he was able by 1891 to identify the structures of all isomers of the naturally occurring D-glucose.

To enable representation of these isomers on the flat surface of a page, Fischer developed a notation system (Fischer projections). Fischer projections denoted right- and left-handed isomers. These were called D (dextrorotatory) and L (levorotatory), respectively, and the compound glyceraldehyde (which exists in two forms) was used as a reference.



$H-\overset{CHO}{\underset{CH_2OH}{C}}-OH$



$HO-\overset{CHO}{\underset{CH_2OH}{C}}-H$

With the Fischer projections, the constituents on the horizontal lines may be envisioned as coming out of the page, and the vertical constituents, as pointing backward, away from the onlooker. Fischer assumed the D isomer corresponded to the projection in which the OH group was to the right of the CH_2OH group. This assignment (which was a guess) was proven correct in 1954 when the orientations in space of the glyceraldehyde stereoisomers were established by x-ray analysis.

Fischer's identification of the stereoisomers of D-glucose (naturally occurring d-glucose was the sugar that Fischer worked with) was important validation of the ideas of van't Hoff.

In 1899 Fischer turned his attention to the study of proteins, wishing to understand their chemical structures. It was known at that time that proteins were composed of amino acids, and thirteen naturally occurring ones were identified. Fischer was able to isolate via the hydrolysis of proteins three additional naturally occurring amino acids: valine, proline, and hydroxyproline. Amino acids exhibit stereoisomerism, and Fischer was able to separate individual forms from mixtures of stereoisomers for several of these compounds.

Another Fischer achievement was the synthesis of small peptides via the condensation of amino acids. Fischer suggested that there was a common linkage that held pairs of amino acids together in all proteins—the peptide bond. He understood that proteins were tremendously complex, owing to the large number of constituents and the fact of stereoisomerism. By 1916 Fischer had synthesized and characterized 100 peptides, but knew they represented a tiny fraction of what was possible. SEE ALSO Amino Acid; Carbohydrates; Isomerism; van't Hoff, Jacobus.

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Fission ***See Transmutation.***

Fleming, Alexander

SCOTTISH BACTERIOLOGIST
1881–1955

Alexander Fleming will always be remembered for turning a laboratory mishap into one of the great medical discoveries of the twentieth century. His discovery of penicillin in 1928 laid the foundation for modern antibiotic therapy and earned him a share of the 1945 Nobel Prize in physiology or medicine.

Fleming was born on August 6, 1881, at Lochfield near Darvel in Ayrshire, Scotland. He attended elementary and secondary school in Scotland and then moved to London to attend the polytechnic school. He graduated with distinction in 1906 from St. Mary's Medical School, London University, received a graduate degree in bacteriology from St. Mary's in 1908, and lectured there until 1914. After serving as a captain in the Army Medical Corps during World War I, Fleming returned to St. Mary's in 1918.

Throughout his career Fleming was intensely interested in naturally occurring antibacterial substances, and penicillin was actually the second antibiotic that he discovered. In 1922 he described the antibacterial properties of lysozyme, a substance found in egg whites, mucus, and tears, which lysed, or dissolved, certain bacteria. Fleming found that lysozyme could turn a thick, milky white suspension of bacteria into a clear solution in a matter of seconds.

Unfortunately, lysozyme failed to destroy bacteria that caused human diseases and was never used as a medicine. Despite the limited utility of lysozyme, Howard Florey and Ernst Boris Chain of Oxford University later determined both its structure and the mechanism by which it destroys bacteria. These two scientists would figure prominently in Fleming's greatest discovery: penicillin.

Fleming freely admitted that he was not looking for a new antibiotic when he discovered penicillin in 1928. In fact, he was working on a problem unrelated to antibiotics when he returned to his lab from a month-long vacation and observed that a blue mold, or fungus, had grown on a discarded **culture** plate of *Staphylococcus aureus* (a common bacteria that causes many diseases in humans). Fleming further observed that a bacteria-free zone had developed around the mold. The once thick cultures of bacteria near the mold had become translucent, or almost clear, and evidently a substance produced by the mold had diffused through the culture medium and killed the bacteria.

culture: living material developed in prepared nutrient media

Scottish bacteriologist Sir Alexander Fleming, corecipient, with Ernst Boris Chain and Sir Howard Walter Florey, of the 1945 Nobel Prize in physiology or medicine, "for the discovery of penicillin and its curative effect in various infectious diseases."

The extraordinary appearance of the bacteria-free zone interested Fleming, so he set out to isolate the mold in pure culture and to determine some of its properties. Fleming classified the mold as *Penicillium rubra*, hence, the name penicillin for the active substance.

Fleming tested the purified mold against other bacteria and observed that some bacteria grew right up to the mold, while others grew only to within a few centimeters of it. He tested other molds for their ability to kill sensitive bacteria and found none. Fleming then grew the mold in a liquid medium and determined that the mold **excreted** penicillin into the culture medium. When he tested the medium against common bacteria, Fleming found that the growth of many disease-causing bacteria was inhibited. He even injected the medium into mice and observed no toxic effects from the new substance.

excrete: to eliminate or discharge from a living entity

Although Fleming was convinced that penicillin had enormous potential value in medicine, he was unable to produce enough of it to demonstrate its value to the medical community. He published his findings in 1929, and penicillin seemed destined for obscurity. But in 1938, Florey and Chain began to reinvestigate penicillin and eventually produced enough pure material to demonstrate that Fleming's assertions were correct. Penicillin has indeed had enormous value in the treatment of infections worldwide. SEE ALSO ANTIBIOTICS; PENICILLIN.

Thomas M. Zydowsky

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9
F
FLUORINE
18.9984

Fluorine

MELTING POINT: −223°C
BOILING POINT: −188°C
DENSITY: 1.696 g/cm^3
MOST COMMON IONS: F^-

Fluorine is a chemical element that in pure form occurs as a dimer of two fluorine atoms, F_2. The fluorine atom has the ground state electron configuration $1s^2 2s^2 2p^5$. There is only one stable, naturally occurring **isotope** of fluorine: ^{19}F. However, the radioactive isotopes ^{17}F, ^{18}F, and ^{20}F are known. The inclusion of the isotope ^{18}F (half-life 110 minutes) in bioorganic molecules is an important noninvasive technique used in the study of living tissue by positron emission tomography.

isotope: form of an atom that differs by the number of neutrons in the nucleus

Fluorine is the most **electronegative** element. It is the lightest and most reactive element in the **halogen** family. Fluorine is a poisonous, corrosive, pale yellow gas with an acrid odor. It is the most powerful oxidizing agent known. The low F–F bond energy and the high energy of bonds between

electronegative: capable of attracting electrons

halogen: element in the periodic family numbered VIIA (or 17 in the modern nomenclature) that includes fluorine, chlorine, bromine, iodine, and astatine fluorine and other elements combine to make reactions of fluorine exothermic.

Elemental fluorine was first prepared by Henri Moissan in France in 1886 via the electrolysis of anhydrous hydrogen fluoride in the presence of potassium fluoride. Fluorine forms compounds with all of the elements except helium, neon, and argon. In nature, fluorine is primarily found in the minerals fluorospar (CaF_2), cryolite (Na_3AlF_6), and fluoroapatite ($CaF_2 \cdot 3Ca_3(PO_4)_2$), together comprising 0.065 percent of Earth's crust (making fluorine the thirteenth most abundant element). These minerals are widely used as electrolytes in the preparation of aluminum, as fluxes in the **metallurgy** of iron, and as additives in ceramics.

Other important inorganic compounds of fluorine include uranium hexafluoride, UF_6, a **volatile** substance that was used to separate ^{238}U from the **fissionable** ^{235}U by gaseous diffusion in the **Manhattan Project**. Sodium fluoride, NaF, is often added to drinking water and to toothpaste in order to reduce the incidence of tooth decay.

When hydrogen is replaced by fluorine in organic compounds, the properties of the compounds are substantially altered. The new compounds have increased chemical, thermal, and oxidative stability. Low molecular weight **chlorofluorocarbons**, known as Freons, are nonflammable, dense, nontoxic compounds particularly useful as refrigerants and blowing agents. Substitutes for these ozone-depleting compounds are being developed.

Teflon (polytetrafluoroethylene) is a chemically **inert** polymer used to create nonstick frying pans. Polytetrafluoroethylene can be modified to form a coating, Gore-Tex, which allows the passage of water vapor, but not liquid water, and is used in many articles of clothing. Polymeric perfluorinated ethers are widely used as high performance oils and lubricants.

The introduction of one to three fluorine atoms to large organic molecules, such as steroids, has been shown to modify the biological activity of these molecules. Many of these fluorine-containing compounds that are useful as pharmaceutical agents have been prepared. The compound 5-fluorouracil is a widely used anticancer agent. Prozac (containing fluorine) is a well-known antidepressant drug. In addition, agrochemists have developed many herbicides (e.g., trifluralin), insecticides (e.g., diflubenzuron), and fungicides (e.g., flutriafol) that incorporate fluorine. Fluorinated dyestuffs and fluorinated liquid crystals have also found commercial use. SEE ALSO ATMOSPHERIC CHEMISTRY; HALOGENS; OZONE.

Suzanne T. Purrington

metallurgy: the science and technology of metals

volatile: low boiling, readily vaporized

fissionable: of or pertaining to unstable nuclei that decay to produce smaller nuclei

Manhattan Project: government project dedicated to creation of an atomic weapon; directed by General Leslie Groves

chlorofluorocarbon (CFC): compound that contains carbon, chlorine, and fluorine atoms; it can remove ozone in the upper atmosphere

inert: incapable of reacting with another substance

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Food Preservatives

Most foods contain enzymes or natural chemicals, such as acids or alcohols, that cause them to begin to lose desirable characteristics almost immediately after harvest or preparation. In addition, a host of environmental factors, such as heat and the presence of microorganisms, acts to change foodstuffs in ways that may harm the food product. Food preservation traditionally has three goals: the preservation of nutritional characteristics, the preservation of appearance, and a prolongation of the time that the food can be stored. Traditional methods of preservation usually aim to exclude air, moisture, and microorganisms, or to provide environments in which organisms that might cause spoilage cannot survive.

Ancient peoples are known to have had dried fruits, vegetables, and meats. The pemmican of Native Americans and the jerky consumed by present-day campers and hikers are both prepared by drying. The drying process can include smoking, which may actually add antibacterial agents. The processes of dehydration and freeze-drying, used today to produce such foods as powdered coffee and soup, are variations of drying.

Among the earliest preservatives were sugar and salt (NaCl), which produced food environments of high osmotic pressure that denied bacteria the aqueous surroundings they needed to live and reproduce. Jams and jellies are preserved as solutions of high sugar content, and many meats (e.g., hams) and fish are still preserved by salting. Unlike other microorganisms, molds can often withstand the effects of high salt or sugar concentrations in foods. Fortunately, they seldom cause illness.

paraffin: saturated aliphatic hydrocarbon (alkane), or hydrocarbon wax

metal: element or other substance the solid phase of which is characterized by high thermal and electrical conductivities

Early methods of air removal included the sealing of foods inside containers (such as jars), or the covering of food surfaces with hot **paraffin**. The invention of canning by Nicolas Appert enabled commercial preparations of foodstuffs. In response to a prize offered by Napoléon in 1795, Appert developed a method of canning and preserving fruits and vegetables in glass containers for sea voyages. His process was used commercially in 1910 by Peter Durand in England, using **metal** cans. During the earliest days of canning, some persons (including some Arctic explorers) probably died as a result of exposure to the lead that was once used to solder cans. Modern techniques of air removal include vacuum sealing and the use of plastic wrappings.

Along with cooking, which kills most bacteria, freezing stops or slows bacterial growth as well as changes in foods brought about by enzymes present in the foods. Unlike the slower freezing of foods in homes, quick freezing in commercial processing enables foods to retain more of their natural appearance and taste.

vitamins: organic molecules needed in small amounts for the normal function of the body; often used as part of an enzyme catalyzed reaction

Chemical preservatives include free radical scavengers (also known as antioxidants), such as **vitamin** C and compounds such as BHA (butylated hydroxyanisole), and bacterial growth inhibitors, such as benzoic acid, sulfur dioxide, and sodium nitrite ($NaNO_2$). Ethanol (CH_3CH_2OH) has long been used as a preservative, both of itself (as in wine), and of other foods (e.g., fruits stored in brandy). Some chemical preservatives may be harmful: Sulfur dioxide (often used to preserve wines) is irritating to the bronchial tubes of persons who have asthma, and nitrites have been implicated as carcinogens.

After Louis Pasteur proved that it was the presence of bacteria that caused food to spoil, there was a tendency to consider all microorganisms harmful. But in fact, microbial action is responsible for the production and preservation of some foods. The action of microbes is a part of the production of cheese and some flavoring agents. Sauerkraut is both processed

Nitrates are a common preservative in luncheon meats.

and preserved by lactobacilli, and yeast cells ferment sugars, producing alcohol, which may add zest to beverages as well as help to preserve them.

The irradiation of foods has the advantage of enabling food packaging and preparation in which there is less person-to-food contact, thus decreasing the possibility of contamination and decreasing the need for chemical preservatives, some of which may be harmful. The ionizing radiation that is used to irradiate foods, wherein the foods are exposed to bursts of high-intensity x rays or streams of electrons, disrupts bacterial **DNA**. Some persons have objected to the irradiation of foods because of an (unfounded) fear of radioactivity. As pathogens such as virulent strains of coliform bacteria have caused food poisoning, the irradiation of animal carcasses and, in particular, of hamburger during its preparation has become more desirable. Irradiation currently extends the shelf lives of foods such as strawberries. Irradiation does not make foods radioactive, but may cause changes in food color or texture. SEE ALSO Ascorbic Acid; Carcinogen; Kinetics; Pasteur, Louis.

DNA: deoxyribonucleic acid—the natural polymer that stores genetic information in the nucleus of a cell

Dan M. Sullivan

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Forensic Chemistry

Few processes are more important to society than solving crimes, both to protect the public from criminals and to protect the innocent from unjust punishment. Very often, the strength of a prosecution rests on the ability of law enforcement personnel to connect the accused with the victim by matching physical evidence from the crime scene or victim with trace evidence found on or about the person accused of the crime. Forensic investigators consult a wide range of experts who analyze evidence collected at crime scenes and brought to the crime laboratory for examination. Forensic chemists perform specialized analyses to identify materials and learn the nature of such evidence. A highly trained forensic chemist can determine the composition and nature of materials and predict the source as well as matching sample against sample. Modern chemistry employs a wide range of analytical techniques along with traditional methods of analysis.

Physical evidence collected at crime scenes is sealed in special containers to prevent contamination and degradation and is catalogued carefully. A **chain of custody** is established and documented as the evidence is sent to a forensic laboratory. At the laboratory, the evidence is examined by personnel trained in one of several fields: Forensic serologists examine body fluids, forensic pathologists examine human remains, firearms technicians classify and test firearms and explosives, and forensic chemists determine the composition and identity of materials.

chain of custody: sequence of possession through which evidentiary materials are processed

The History of Forensic Chemistry

Poisons were employed by early Egyptians and ancient Greeks and Romans. Democritus was probably the first chemist to study poisons, and he communicated some of his findings to **Hippocrates**. Poisons were used both for murder and as a means of execution; the philosopher **Socrates** was condemned to death by drinking **hemlock**. Ancient Roman civilization had laws against poisoning in 82 B.C.E. Before the development of systematic, scientific criminal investigation, guilt was determined largely by circumstantial evidence and hearsay. **Arsenic** was a popular poison in Roman times. It was referred to as inheritance powder in early France. The Blandy trial of 1752 was the first instance of an actual chemical test for poison, and the Marsh test, developed in 1836, was the first reliable analysis that could show scientifically that arsenic was present in the body of a victim.

Hippocrates: Greek physician of fifth century B.C.E. known as "Father of Medicine"

Socrates: Greek philosopher, ca. 470–399 B.C.E.

hemlock: poisonous herb of the genus Conium

arsenic: toxic element of the phosphorus group

Every chemist is schooled in general, organic, and analytical chemistry, but forensic chemists also specialize in specific areas of expertise. For example, an inorganic chemist may examine traces of dust by using **microchemistry** to identify the chemical composition of tiny particles. Another chemist might employ thin-layer **chromatography** during the analysis of

microchemistry: chemical investigation carried out on a small scale

chromatography: the separation of the components of a mixture in one phase (the mobile phase) by passing it through another phase (the stationary phase) making use of the extents to which the components are absorbed by the stationary phase

Forensic scientists examine evidence from crime scenes in an effort to solve crimes. This scientist is removing a piece of blood-stained material gathered at a crime scene for DNA testing.

blood or urine for traces of drugs, and still another might use chemical reactions in test tubes to identify larger samples of compounds.

What Do Forensic Chemists Do?

Forensic chemistry encompasses organic and inorganic analysis, **toxicology**, arson investigation, and **serology**. Each method of analysis uses specialized techniques and instrumentation. The process may be as simple as setting up a density gradient column to compare soil samples or as complicated as using a mass spectrometer or **neutron activation analysis** to characterize an unknown substance.

toxicology: division of pharmacology dealing with poisons, their identification, detection, effects on the body, and remedies

serology: the study of serum and reactions taking place within it

neutron activation analysis: method for detecting traces of elements by bombardment with high-flux neutrons and then measuring the decay rate of the radioactive products

A wide array of laboratory techniques and instrumentation is used in forensic studies. This includes ultraviolet, infrared, and visible spectrophotometry; neutron activation analysis; gas chromatography and mass spectrophotometry; high pressure liquid chromatography; and atomic absorption spectrophotometry. The techniques and instrumentation chosen depend on the type of sample or substance to be examined.

The fact that most samples examined are not pure substances, but are often mixed with dirt or debris, presents a major challenge to the forensic chemist. This may also be an advantage, as every substance collected at a crime scene is a unique mixture of chemical compounds that can ultimately be identified. Arsonists, for example, often use accelerants such as gasoline or kerosene to speed **combustion** and spread flames in the interior of a building. A forensic chemist may collect samples of burned and unburned materials, extract the **volatile** hydrocarbons, and separate the components for analysis by gas chromatography.

combustion: burning, the reaction with oxygen

volatile: low boiling, readily vaporized

Analytical Techniques and Instrumentation

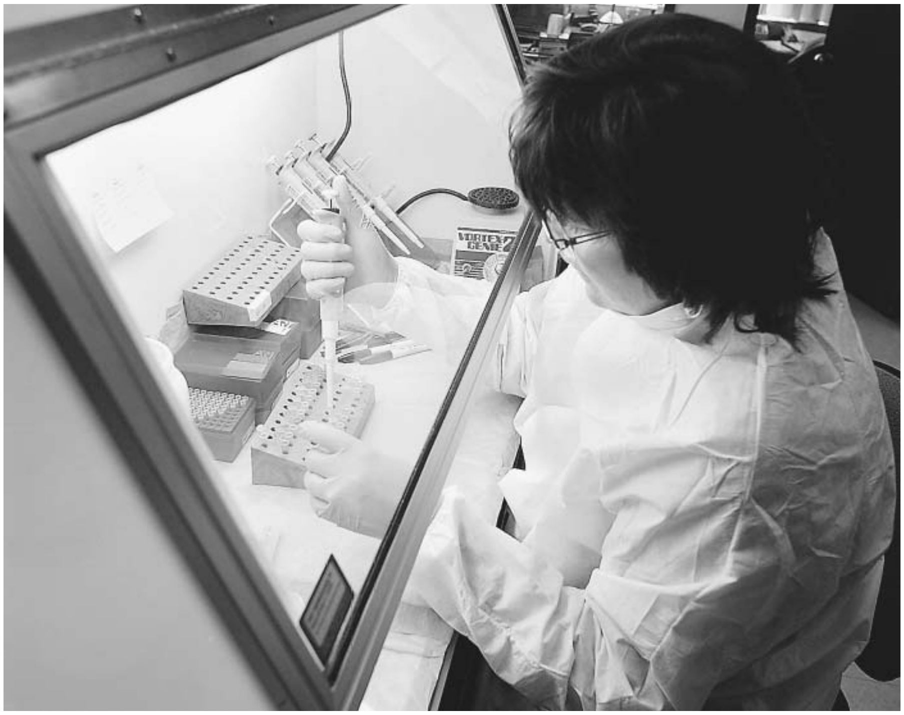
The gas chromatograph (GC) separates volatile substances into separate components by passing the volatile materials through a long absorbent column. The technique is highly reproducible and reliable; since each sample is likely to contain a definite number and type of impurities, it may provide a close match of the unknown accelerant to a known source such as a gasoline tank or hardware store. It may be necessary to vaporize a tiny sample of the material to provide volatile gases for analysis. The components of the vapor are then passed through the column and separated into a number of components, each of which can be captured and analyzed. In most cases, the accelerant will be mixed with portions of burned paint or building materials, making simple identification by examination impossible, but the ability of the GC to separate tiny portions helps in identification.

The GC is often connected to a mass spectrometer. Mass spectrometry (MS) breaks samples apart and separates the ionized fragments by mass and charge. Vast libraries of comparison fragments make computer-aided identification of materials possible even when the sample is very small. Most forensic laboratories have access to a combined gas chromatograph/mass spectrometer (GC/MS). High pressure liquid chromatography (HPLC) separates many types of drugs and may also be combined with MS.

Analysts may use several types of spectrophotometry. A typical spectrophotometer consists of a light source that provides light of a known wavelength; a holder to position solid, liquid, or gaseous samples; and a system of lenses and photocells that compare light shining on the sample with light passing through. A decrease in the intensity of light passing through the substance indicates the presence of materials that absorb light at that wavelength; the absorbance is quantitative and a measure of the concentration of material, and the wavelengths of maximum absorbance are characteristic of the type of material. Infrared spectrophotometry is especially useful for the identification of organic compounds, as bonds between certain atoms readily absorb infrared radiation (IR).

Ultraviolet (UV) spectrophotometry helps distinguish between samples of proteins and nucleic acids such as deoxyribonucleic acid (**DNA**). Atomic

DNA: deoxyribonucleic acid—the natural polymer that stores genetic information in the nucleus of a cell



At the Colorado Bureau of Investigation in Boulder, lab agent Kathy Dressel works on DNA evidence in the JonBenet Ramsey murder investigation.

absorption spectrophotometry provides ways of determining absorption and emission spectra, useful tools in the analysis of **metals** such as bullet fragments.

metal: element or other substance the solid phase of which is characterized by high thermal and electrical conductivities

nuclear: having to do with the nucleus of an atom

Nuclear magnetic resonance spectrophotometry (NMR) makes use of the fact that nuclei of some molecules absorb radio frequency radiation in strong magnetic fields. Nuclei in certain molecules absorb radiation at characteristic frequencies, making the identification of even tiny or impure samples possible. X-ray analysis allows the forensic investigator to visualize foreign objects within the body.

In neutron activation analysis, a beam of neutrons from a nuclear reactor is directed at a sample of test material. The material becomes temporarily radioactive, emitting γ-rays that are characteristic of the composition; analysis of the γ-radiation provides a highly accurate and reproducible determination of the content of the sample. This technique has made possible the determination of arsenic in the hair of corpses buried for hundreds of years. In one case, the body of an Arctic explorer who had died under suspicious circumstances during the 1870s was found buried in a coffin surrounded by ice. Neutron activation analysis of hair from the body showed that hair that was several centimeters long contained little arsenic, but that shorter hair closer to the scalp (which had grown in the few days before death) contained high levels of arsenic, indicating that death was probably caused by arsenic poisoning.

Often, the presence of very small impurities makes comparison possible. For example, cars are painted with paints prepared to certain specifications of color and composition, and pigments and binders used vary from one manufacturer to another and even between models from the same distributor. A small sample of paint left at the scene of an accident may be checked for color by spectrophotometry and then analyzed for composition. Perpetrators of many hit-and-run crimes have been convicted on the basis of combined GC/MS analysis of paint chips.

Residues left by burning powder from firearms consist of patterns of particles that have both characteristic physical and chemical properties. Burned powder, for example, usually contains traces of nitrites that yield chemical reactions and traces of metals such as barium that are often present in primers. Both chemical reactions and microscopic analysis (including electron microscopy) are employed in the identification of powder residues on clothes and skin. An early method for detecting gunshot residue on the hands of suspects involved coating the hand with melted **paraffin**, allowing the paraffin to cool, and then stripping it off. Gunshot residues transferred from skin to paraffin turned blue or green in the presence of diphenylamine, but many common substances such as urine gave a false positive test. The Greiss **reagent** is much more definitive, and additional tests can identify traces of lead around bullet holes. Even microscopic particles are found to have definite compositions and can be unequivocally identified.

paraffin: saturated aliphatic hydrocarbon (alkane), or hydrocarbon wax

reagent: chemical used to cause a specific chemical reaction

Toxicology

Toxicologists examine a wide range of materials such as blood stains, urine, and blood gases for traces of poisons or drugs. Many businesses now require the drug screening of employees; it is the responsibility of the technician to distinguish between the presence of illegal drugs and **metabolites** from foods such as poppy seeds. Such tests may be as simple as paper or thin-layer chromatography or as complicated as gas chromatographic or electrophoretic and serological analysis of a blood sample. Following death by unknown cause, samples of the victim's lungs, blood, urine, vitreous humor, and stomach contents are examined for traces of poisons or medication. Insects found on or near corpses are also collected and examined; they may actually absorb traces of drugs or poisons from the body, and in fact, traces of poisons sometimes are found in the surrounding insects long after concentrations in the body have fallen below detectable limits.

metabolites: products of biological activity that are important in metabolism

Forensic biochemists perform blood typing and enzyme tests on body fluids in cases involving assault, and also in paternity cases. Even tiny samples of blood, saliva, or semen may be separated by **electrophoresis** and subjected to enzymatic analysis. In the case of rape, traces of semen found on clothing or on the person become important evidence; the composition of semen varies from person to person. Some individuals **excrete** enzymes such as acid phosphatase and other proteins that are seldom found outside seminal fluid, and these chemical substances are characteristic of their semen samples. The presence of semen may be shown by the microscopic analysis for the presence of spermatozoa or by a positive test for prostate specific antigen.

electrophoresis: migration of charged particles under the influence of an electric field, usually in solution; cations, positively charged species, will move toward the negative pole and anions, the negatively charged species, will move toward the positive pole

excrete: to eliminate or discharge from a living entity

In cases of sexual assault, tiny samples of DNA in blood, semen, skin, or hair found on the victim may be purified and the amount of DNA increased by the use of a polymerase chain reaction to produce quantities large enough to analyze. Since DNA is as specific to a person as fingerprints, matching the DNA of a perpetrator to a sample found on a victim is considered to be proof of contact. The Federal Bureau of Investigation (FBI) is currently in the process of establishing a national Combined DNA Index System (CODIS) that will collect data from many states and law enforcement agencies and index it so that particular DNA patterns from evidence collected at many crime scenes can be compared and matched. Many perpetrators of crimes have been convicted and many innocent persons set free after years in prison as a result of DNA analysis.

Testing for Alcohol

Accidents caused by intoxicated drivers kill nearly 15,000 persons a year in the United States alone (almost half of fatal auto accidents are alcohol-related), so a Breathalyzer kit is standard equipment in most police squad cars or state patrol vehicles. Breathalyzers are used to estimate the blood alcohol content of drivers suspected of being intoxicated; the driver may appear sober, but still have a blood alcohol level above the legal limit. Although it is impractical to take blood samples on the highway, research has shown that the concentration of ethanol in the breath bears a definite relationship to its concentration in blood. Many communities have now set a legal limit of 0.08 percent (meaning that 100 milliliters [3.38 fluid ounces] of blood would contain 0.08 grams [0.0028 ounces] of ethanol). In fact, authorities now consider that a person's driving ability is probably impaired at a blood ethanol level of 0.05 percent.

Several types of analytic devices are available to administer Breathalyzer tests. One test makes use of a portable infrared spectrophotometer, another uses a fuel cell, and the most common test employs several glass or plastic tubes and some common chemical reagents. The person being tested blows through a tube, which bubbles the breath through a solution of chemicals containing sulfuric acid, potassium dichromate, water, and silver nitrate. **Oxidation** of the alcohol results in the reduction of dichromate ion to chromic ion, with a corresponding change in color from orange to green. An electrical device employing a photocell compares the color of the test solution with a standard solution, giving a quantitative determination of the alcohol content. The test provides a quick and reproducible determination of the amount of alcohol in a person's breath and is a numerical measure of the amount of alcohol in the bloodstream. Use of a chemical test helps to avoid subjective opinions of sobriety and provides reliable evidence for court proceedings. The test can be readily and quickly administered by trained law enforcement personnel, but forensic chemists test and calibrate the equipment and testify to its accuracy.

oxidation: process that involves the loss of electrons (or the addition of an oxygen atom)

Fingerprinting

Fingerprints on smooth surfaces can often be made visible by the application of light or dark powder, but fingerprints on checks or other documents are often occult (hidden). Occult fingerprints are sometimes made visible by the use of ninhydrin, which turns purple due to reaction with amino acids present in perspiration. Fingerprints or other marks are also sometimes made visible by exposure to high-powered laser light. Some fingerprints can be treated with chemical substances, resulting in a pattern that fluoresces when exposed to light from lasers. Cyanoacrylate **ester** fumes from glue are used with fluorescent dyes to make the fingerprints visible.

ester: organic species containing a carbon atom attached to three moieties: an O via a double bond, an O attached to another carbon atom or chain, and an H atom or C chain; the R(C═O)OR functional group

Forensic chemists are usually employed by laboratories in law enforcement agencies or by private testing laboratories and are often called on to provide testimony in court proceedings as expert witnesses. In these cases, the chemist may compare evidence in the case in question to a large number of similar cases he or she has examined and is often asked to give an expert opinion as to the quality of the evidence. Since forensic chemists usually have both a bachelor's degree in chemistry and an advanced degree in forensic science, their academic credentials, along with years of experience and the ability to compare the case in question with a large number of other cases, renders the testimony both valuable and believable. SEE ALSO Analytical Chemistry; Arsenic; Careers in Chemistry.

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Formulation Chemistry

Formulation chemistry is the branch of manufacturing that addresses substances that do not react with each other, but have desirable properties as a mixture. These products include paints, varnishes, cosmetics, petroleum products, inks, adhesives, detergents, pesticides, and a broad range of household products.

Successful formulation requires a blend of art and science. Components are chosen for compatibility rather than reactivity. Formulation chemists think in terms of kilograms or tons rather than moles and place more emphasis on solubility than molecular weight.

Paints

Paints are suspensions of pigments, binders, drying agents, and vehicles. Vehicles are solvents in which the pigment is mixed. Pigments are powders made from insoluble chemicals, such as titanium dioxide, that give color to the preparation. Titanium and zinc oxides have largely replaced lead pigments in paint.

Binders bind pigments to surfaces. They solidify by drying, cooling, or reacting to produce polymers. Acrylic paints use polymer resins as vehicles. They can be thinned with water, but dry readily. Drying agents aid in the evaporation of a vehicle or help paint mixtures to polymerize.

Cosmetics

The cosmetic industry provides a wide assortment of formulated products. A typical bathroom contains a full range of perfumes, moisturizers, rouge, lipstick, antiaging skin products, face powder, emollients, nail polish, sunscreen, hair conditioning and coloring products, aftershave, drugs, and deodorants as well as medications.

Nail polish consists of flexible lacquers, pigments such as organic dyes, iron or chromium oxides, and ultramarine blue along with drying agents and binders or vehicles such as ethyl acetate that evaporate on drying. Nail polish remover is usually an organic solvent such as acetone or ethyl acetate.

Perfumes have been used since the days of ancient Egypt. Perfume bottles are among the most ancient glass items recovered in Asia, where perfumes were probably first extracted from plant materials such as roses, geraniums, or lemon oils. Later processes blended animal products such as ambergris and musk. The first perfumes were probably developed to mask the odors of disease or poor hygiene. Modern perfumes include components blended to produce a combination of scent that will last for several hours and provide a combination of notes (or fragrance impressions). The first note is the odor perceived when one sprays or applies perfume from a bottle. The second note or odor develops after the perfume has made contact with the skin, and the third note is the ability of fragrance to linger.

Most perfume preparations are not patented, but considered trade secrets, so manufacturers are not required to list their ingredients. High-quality perfumes are mixtures of substances that appeal to certain individuals. Typical ingredients include extracts of flowers and fragrances such as valerian, lavender, chamomile, passionflower, ylang-ylang or vanilla, geranium, mint, lemon, fixatives such as ambergris or musk, and water or alcohols. The formulation of perfumes is an art practiced by technicians who have developed abilities to perceive individual and blended fragrances. In addition to products for personal application, perfumes are used in numerous cleaning products.

Detergents

Detergents are among the most common household products and act as **wetting agents**. Water is a polar compound that readily dissolves most salts and polar compounds such as sugar. **Nonpolar** solvents such as gasoline or carbon **tetrachloride** (CCl_4) do not mix well with water, but dissolve nonpolar substances such as grease or oil.

wetting agent: molecule that, when added to a liquid, facilitates the spread of that liquid across a surface

nonpolar: molecule, or portion of a molecule, that does not have a permanent, electric dipole

tetrachloride: term that implies a molecule has four chlorine atoms present

Shampoo contains a mixture of ingredients, including detergents, that allow water to wet the nonpolar oils found in bodily secretions such as sebum, the oily substance which holds dirt and dead skin in hair. Common anionic detergents include sodium or ammonium lauryl sulfates. Cationic detergents, which act to condition hair as well remove dirt and oil from it, include alkyl ammonium compounds such as stearylammonium chloride or sulfate. Other components of shampoo include **surfactants** such as polyethylene glycol, antifoaming agents, thickeners, antistatic agents, and pH balancers. Formulation chemists add coloring or pearlizing agents and perfumes to shampoos to make them more attractive.

surfactants: surface-active agents that lower the surface tension of water; e.g., detergents, wetting agents

Much of the scum that forms on the walls of showers is a soap film, actually calcium or magnesium salts of fatty acids. Most soaps are sodium or potassium salts of fatty acids that function well as surface active or wetting agents, but calcium and magnesium ions in hard water form insoluble compounds with these fatty acids that dull shower walls. Shower cleaners typically contain chelating agents such as ethylenediamine tetraacetate (EDTA) that form soluble complexes with the ions. In addition, a surfactant such as an ethylene glycol ether wets the wall so water droplets run off. Isopropyl alcohol is a solvent both for the ingredients and for substances such as oils that are not water-soluble.

Sunscreen

A well-designed sunscreen does two things: It blocks harmful ultraviolet (UV) rays and allows the skin to tan. UV rays carry high energy and are suspected to cause cancer by damaging **DNA**. In addition, excess UV exposure causes increased wrinkling of the skin. Zinc oxide (ZnO) and titanium dioxide (TiO_2) are the long-term ingredients of most sunblockers, considered broad-spectrum agents because they block all UV light. Many sun worshipers or outdoors enthusiasts apply a coat of reflective zinc oxide and cream to their noses and ears for extra protection.

DNA: deoxyribonucleic acid—the natural polymer that stores genetic information in the nucleus of a cell

High energy in sunlight comes in two portions: UV-A (320–400 nanometers, or 1.2×10^{-5}–1.6×10^{-5} inches) and UV-B (290−320 nanometers, or 1.1×10^{-5}–1.2×10^{-5} inches). Since the light of shorter wavelength radiation is more energetic, UV-B causes burning, while UV-A promotes tanning. Although not as likely to result in sunburn as UV-B, exposure to UV-A does cause eventual wrinkling and aging of the skin. p-Aminobenzoic acid (PABA) in sunscreen absorbs the energy of UV-B while allowing UV-A to pass through. Other aromatic organic compounds such as benzophenone or oxybenzone are used with or in place of PABA. In the formulation process chemists must choose emollients and sunscreens that remain dispersed without precipitating from solution and feeling gritty.

Although probably harmless at the low concentrations used, most aromatic organic compounds pose some risk of cancer or of interference with bodily hormones, but this risk is probably lower than that of skin cancer or wrinkles. New technology allows encapsulation of the active ingredients of sunblockers in tiny polymer bags that keep the chemical agents away from the skin.

Dihydroxyacetone (DHA) acts as a self-tanning agent to give sunless tans. The browning action probably involves the reaction of DHA with free amino acids to form melanoidins. Melanoidins probably offer only slight UV protection.

Ancient Romans were aware of the bleaching effects of sunlight and used this and other processes to lighten hair. Modern bleaching is done with oxidizing agents such as hydrogen peroxide that destroy melanin, the natural pigment of hair. Hair containing no pigment is light-colored or white.

Hair Coloring Products

Hair coloring products are either temporary or permanent. Temporary hair colors attach to the surface of hair and wash out after repeated shampoos.

A dye is considered permanent if it penetrates into the hollow hair shaft. Coloring of hair starts with a treatment of substances such as hydrogen peroxide and ammonia. The ammonia causes hair shafts to swell and open, allowing dye **intermediates** and couplers to penetrate. Dyes applied during the second step of coloring react with the precursors to form pigments that remain in the hair.

intermediate: molecule, often short-lived, that occurs while a chemical reaction progresses but is not present when the reaction is complete

Melanin compounds may appear brown, black, or red. The type of melanin determines hair color, and the density of melanin granules determines the shade. Dark shades of dyed hair contain higher concentrations of dyes. Most hair colors are combinations of organic compounds chosen to produce particular shades. Resorcinol produces a yellow color; aminohydroxytoluene produces a redder hair, and nitrophenylenediamine dye results in very red hair. Graded dyes favored by men often contain lead acetate. The lead ions penetrate into hair and form lead sulfide (PbS), a dark-colored compound.

Deodorants

Deodorants and antiperspirants are frequently compounded together. Deodorants seldom actually remove odor; they simply mask odors or inhibit the microorganisms that cause body odor. Deodorants include several strong perfumes, often with minty or musky odors. Odors can be lessened somewhat by decreasing perspiration. Most underarm perspiration comes from the apocrine or eccrine glands. Perspiration probably functions primarily to cool the skin and get rid of excess heat, but may also carry pheromones and fatty acids and **excrete** excess salt. The active ingredients of antiperspirants are usually aluminum salts such as aluminum chloride ($AlCl_3$). Aluminum ions are absorbed by cells in the epidermis that squeeze the sweat gland ducts closed. Talcum powders may be used to absorb excess perspiration.

excrete: to eliminate or discharge from a living entity

Gasoline

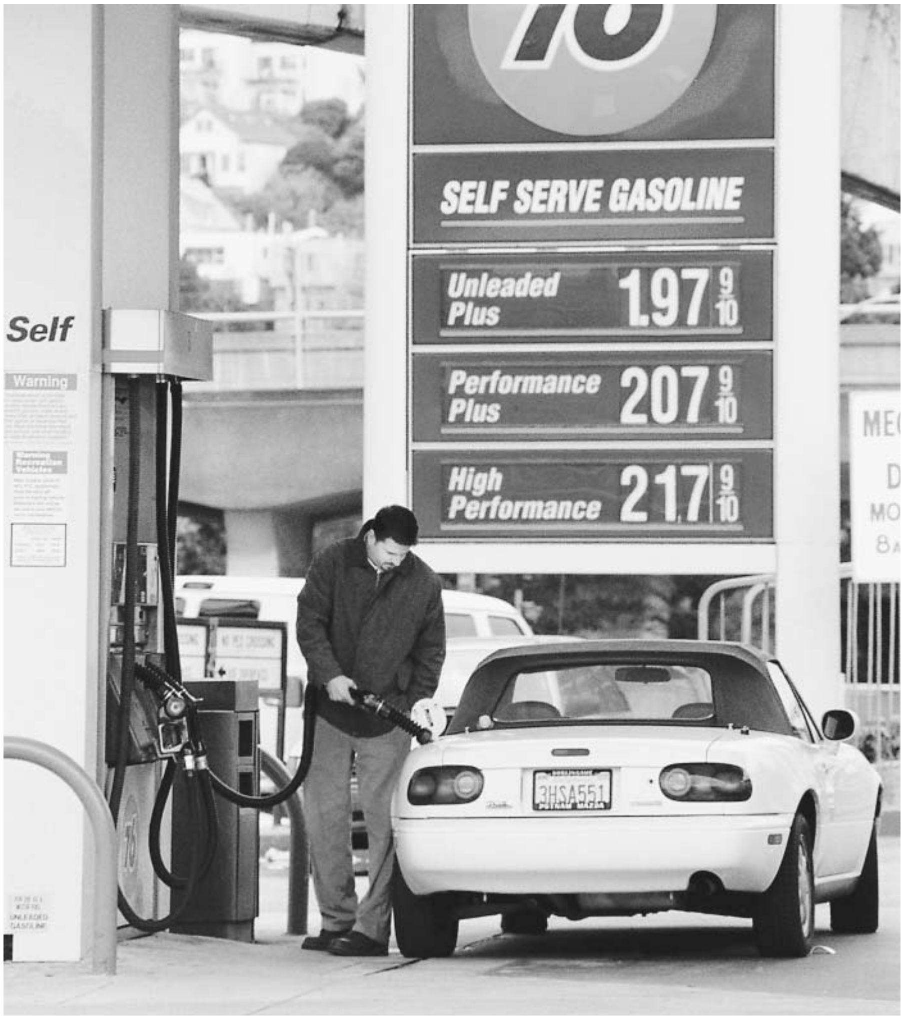
Civilization runs on gasoline. Gasoline is a solution of hydrocarbons chosen by composition and boiling point as a fuel for internal **combustion** engines. Petroleum from oil wells is a mixture of thousands of different hydrocarbons that must be refined and separated into useful components. In general, the longer and larger molecules vaporize at higher temperatures. Gasoline is a mixture of hydrocarbon chains typically seven to eleven carbons long.

combustion: burning, the reaction with oxygen

Gasolines are blended to produce mixtures that vaporize rapidly in carburetors or by passing though fuel injectors. In addition, blends are chosen to give certain octane ratings. The traditional octane rating system compares the knocking characteristics of fuels to *n*-heptane (C_7H_{16}), a fuel that knocks badly and is assigned an octane rating of zero, and isooctane (2,2,4-trimethylpentane, an **isomer** of octane, C_8H_{18}). Isooctane can be used without knocking in high-compression engines, yielding more power than low-octane fuels. The octane ratings of low-octane fuels can be raised by adding branched-chain or cyclic hydrocarbons, or by adding octane enhancers.

isomer: molecules with identical compositions but different structural formulas

The first octane enhancers were lead compounds such as tetraethyl lead (TEL) or tetramethyl lead (TML). A few milligrams of either converted inexpensive, low-octane gasoline into high-test fuels. As the danger of lead to



Gasoline, a mixture of hydrocarbon chains seven to eleven carbons long, is blended for different octane ratings.

the environment and to catalytic converters became apparent, lead compounds were phased out and lead-free gasolines introduced. Typically, lead-free gasoline contains cyclic compounds such as benzene and oxygenated additives such as ethanol, methanol, or methylcyclopentadienyl manganese tricarbonyl (MMT). Oxygenated fuels burn cleaner in cold engines.

Pesticides

Pesticides are chemical agents used to kill pests such as insects, snails, spiders, birds, or fish. Any living thing can be a pest at times; many weeds are simply plants growing in unwanted places, and prairie dogs look cute in the zoo, but their eating habits can cause widespread damage to cropland or livestock. Pesticides are, however, seriously poisonous substances.

Dichlorodiphenyltrichloroethane (DDT) is a halogenated hydrocarbon used during the 1940s to control mosquitoes and other disease vectors. Unfortunately, DDT accumulated in the environment until its high levels in the fatty tissues of birds began to cause thin eggshells and loss of life. Although its use is banned in many countries, including the United States, DDT remains a potent weapon against malarial mosquitoes in other parts of the world.

Organophosphate pesticides act by blocking cholinesterase, an enzyme that breaks down the neurotransmitter **acetylcholine** after a nerve impulse crosses the synapse. Most poisons require a lethal dose that depends on the weight of the animal. Because insects weigh much less than humans, the amount needed to kill an insect may be harmless to us. One early pesticide still in use is nicotine, an active ingredient of tobacco. Potent insecticide solutions can be made by soaking tobacco in water, but the formulation chemist produces safer preparations of standard toxicity. SEE ALSO COSMETIC CHEMISTRY; DETERGENTS; GASOLINE; PESTICIDES; SOLUTION CHEMISTRY.

acetylcholine: neurotransmitter with the chemical forumula $C_7H_{17}NO_3$; it assists in communication between nerve cells in the brain and central nervous system

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Fossil Fuels

Since the beginning of the **industrial revolution**, fossil fuels have been important sources of energy. European industrialization began in the late 1700s in England, and coal soon became a major fuel. In 1850 wood was still the main energy source in the United States. During the latter half of the nineteenth century, the United States and other industrialized nations relied on coal (a fossil fuel) to provide the energy for industrialization. Coal remained the major fuel source for many years, and then, in the latter half of the twentieth century, oil and natural gas became the primary energy sources. The first oil well was drilled in Pennsylvania in 1859.

Industrial Revolution: widespread replacement of hand tools by power-driven machines, beginning about 1750 (especially in England)

In 2000, fossil fuels accounted for almost 90 percent of the world's energy production (see Table 1). **Nuclear** power and hydroelectric plants supplied about 13 percent and geochemical, wind, and solar energy sources supplied only a fraction of 1 percent. **Biomass**, including the burning of wood, is not included in the table because it is so difficult to estimate.

nuclear: having to do with the nucleus of an atom

biomass: collection of living matter

Although coal **combustion** produces substantially greater air pollution problems than does oil or natural gas combustion, because of its great abundance in the United States and other countries (such as Russia), there has been renewed interest in developing technology to burn coal more cleanly. However, all fossil fuels consist mainly of hydrocarbons (compounds that contain only carbon and hydrogen), which, upon complete combustion, yield carbon dioxide, a major greenhouse gas.

combustion: burning, the reaction with oxygen

It is widely accepted in the scientific community that fossil fuels (coal, oil, and gas) have a biological origin and are ultimately derived from the buried remains of plant and animal matter, although some still argue in favor of a nonbiological or inorganic source. It is believed that a small fraction (much less than 1%) of dead plant and animal matter accumulates as deposited matter, is removed from contact with atmospheric oxygen, is subject to elevated temperatures and pressures (inhibiting decomposition by bacteria), and over geological time, is transformed into fossil fuels.

WORLD ENERGY SOURCES IN 2000

Source	Percent of Energy
Petroleum	39
Natural Gas	24
Coal	24
Hydroelectric	7
Nuclear	6

Table 1.

Coal

Coal is considered the remnant of plants that grew in swamps hundreds of millions of years ago, and thus its source is often characterized as *terrestrial*, signifying its association with continental land masses. Terrestrial plant material characteristically contains *lignin*, a carbon-based natural polymer that provides rigidity to nonaquatic plants and enables them to stand upright against the pull of gravity. Lignin is much more resistant to bacterial degradation than other botanical components, such as cellulose, and is considered a significant contributor to the chemical composition of coal.

The extent to which lignin and other plant matter has been metamorphosed by the high temperatures and pressures associated with the gradual burial of this material determines the grade of the coal produced. As the process of coal formation (coalification) proceeds, the product is increasingly characterized by lower moisture content, greater carbon and energy content, and a greater hardness. Lignite is the softest and least metamorphosed type of coal, with a relatively high moisture content, a low fixed carbon (nonvolatile carbon) content, and a low energy content. *Subbituminous* coal is the next highest grade, and upon further coalification it can be transformed to bituminous coal, or ultimately to *anthracite*. Anthracite is the hardest coal, possessing about 95 percent fixed carbon, the lowest moisture content, and the best energy content. Coals from different sources also contain differing amounts of inorganic mineral matter (ash), which remains as a residue upon burning and thus lowers the energy content of the coal. Table 2 compares the compositions of the various types of coal.

One mineral often associated with coal is pyrite, FeS_2. The burning of coal contributes to pollution of the atmosphere, owing to the presence in coal of pyrite and organic sulfur-containing compounds. Coal is commonly burned in power plants that generate electricity, and both the inorganic (pyrite-containing) and organic forms of coal are oxidized to yield sulfur dioxide (SO_2). Sulfur dioxide reacts in air to form sulfuric acid (H_2SO_4), which is a major cause of **acid rain**. Sulfuric acid and sulfur dioxide are also lung irritants, and thus health hazards, and contribute to the corrosion of structures by their acidification of all forms of precipitation (rain, snow, fog, sleet). The impact of the atmospheric precipitation of SO_2 and H_2SO_4 has been minimized by chemical and physical processes that remove inorganic sulfur from coal (desulfurization), and by the use of coals with low sulfur content. One positive effect of higher H_2SO_4 levels in the atmosphere is the increase in cloud cover, due to the hygroscopic (water-absorbing) nature of this acid, and this may help to lower the average surface temperature of the planet—although CO_2 produced as a result of oxidization of the carbon in coal is a major contributor to global warming.

acid rain: precipitation that has a pH lower than 5.6; term coined by R. A. Smith during the 1870s

Table 2.

COAL COMPOSITION

Type of Coal	%C	%H	%O	%N	%Moisture	Heating Value (kcal/kg)
Anthracite	92–95	3–4	2–3	0–2	1–4	7500–8000
Bituminous	75–92	4–6	3–20	1–2	5–30	5000–8000
Lignite	60–75	4–6	17–35	1–2	30–50	3000–4500
Peat*	45–60	3–7	20–45	1–3	70–90	<3000

*Peat is a dark, woody soil that has not yet been coalified to lignite.

Coke

Coal can be transformed into coke and other fuels by various industrial and experimental processes. Coke is produced by the pyrolysis (heating in the absence of air) of coal and is used in the production of iron and steel. The coking procedure removes moisture and other volatile components from coal, yielding an extremely carbon-rich material. Coal can also be transformed (via intrafuel conversion) into relatively clean liquid and gaseous fuels (liquifaction and gasification). However, this is accomplished at high cost—in money and energy.

Petroleum

Petroleum is an extremely complex mixture of hydrocarbons, which can be separated into liquid (oil) and gas fractions. Compared to coal, petroleum being a liquid is easier to transport. It probably originated in marine sediments, in contrast to the terrestrial origins of coal.

Because petroleum varies greatly in composition and distribution throughout the world, elaborate systems of refining and transport have been developed. Major oil fields or giant petroleum fields ("giant" indicating oil fields capable of producing at least 500 million barrels of oil) are found primarily in the Middle East, North and South America, and countries that made up the former Soviet Union. The uneven natural distribution of oil, and the consequent need to transport oil across vast distances, has led to instances of contamination due to oil spills. Coastal waters are particularly vulnerable, not only to oil spills, but also to contamination by bilge water and tank-washing water from commercial oil tankers. Even though it is a major producer of oil, the United States has found it necessary to import significant additional amounts of oil in order to meet ever-increasing industrial and home-related energy demands. Most plastics and other petrochemicals are made from petroleum, along with almost all gasoline, diesel fuel, jet fuel, heating oil, and lubricants. However, Earth's supply of petroleum is limited. Some experts estimate that world production of oil could climax as early as 2004. Although most, if not all, of the major oil-producing fields associated with continental masses have been discovered, and many offshore wells have been drilled, there still may be other major oil discoveries in less accessible areas such as under the ocean—a largely unexplored territory.

Natural Gas

The history of natural gas dates back to 900 B.C.E., when its use was mentioned in China. It was apparently unknown in Europe until 1659, when it was discovered in England. It was not discovered in the United States until 1815 in West Virginia. In the early twenty-first century, natural gas has become the favorite fuel of industrial nations. The United States is the largest producer as well as the largest consumer of natural gas. The largest natural gas reserves are located in Russia, Kazakhstan, and Iran.

Natural gas, which consists mainly of methane (CH_4), can contain up to 20 percent of other gases—mainly ethane (C_2H_6), and possibly propane (C_3H_8), butane (C_4H_{10}), pentane (C_5H_{12}), carbon dioxide (CO_2), and nitrogen (N_2). Some natural gases contain small amounts of hydrogen, argon, carbon monoxide, or even hydrogen sulfide. Certain gas wells in Oklahoma also contain helium. In fact, they are a major source of helium in the United States. Natural gas is also colorless, odorless, and nontoxic but very flammable. (The odor we associate with natural gas is because of a mercaptan added to make gas leaks detectable.) Most natural gas is burned as fuel; however, ethane and the higher alkanes can be separated out and cracked to ethylene and propylene for making plastics. Although it is considered a "clean" and environmentally friendly fuel, compared to oil and coal, it is itself a major greenhouse gas and upon combustion yields carbon dioxide, the other major greenhouse gas. Like carbon dioxide, methane is also a greenhouse gas. However, natural gas fuel is thought to be only a minor contributor to methane in the atmosphere. Methane is constantly being generated by marsh and swamp terrain and by certain animals. Some experts believe that animals are the main source of atmospheric methane.

Other Sources of Fossil Fuels

Oil shales and tar sands also contain significant amounts of hydrocarbon materials that might eventually prove to be important energy sources. Oil shales are fine-grained sedimentary rocks (shales) that contain hydrocarbons that are dispersed within the matrix of the rock. A ton of shale contains from 10 to 100 gallons of kerogen, a waxy material that breaks down to oils when heated in the absence of air. It is estimated that three states (Utah, Colorado, and Wyoming) contain shale bearing more oil than exists in all the proven reserves in the world. Tar sands are the extremely viscous petroleum deposits associated with sedimentary rocks. They are mixtures of clay, sand, and extremely viscous oils called bitumens. The utility of oil shales and tar sands is currently limited, because of problems having to do with hydrocarbon recovery and the disposal of large amounts of inorganic residues. SEE ALSO Chemistry and Energy; Coal; Energy Sources and Production; Gasoline; Industrial Chemistry, Organic; Petroleum.

Mary L. Sohn

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Francium

MELTING POINT: 27°C
BOILING POINT: 677°C
DENSITY: unknown
MOST COMMON ION: Fr^+

87
Fr
FRANCIUM
223

The element francium is named for the country of France and its most stable **isotope** is known as actinium K. Dimitri Mendeleev assigned it the name eka-cesium prior to its actual discovery, although at this time it was also known as russium, virginium, and moldavium. Marguerite Perey, a one-time assistant of Marie Curie, discovered francium in 1939. It is not found in its elemental state and less than one ounce is thought to exist in Earth's crust at any one time.

isotope: form of an atom that differs by the number of neutrons in the nucleus

Although there are a number of isotopes of francium, most decay very rapidly to other elements. Most isotopes with masses of 223 AMU and lower emit **α-particles** (consisting of two protons and two neutrons) to become astatine. Some low mass francium isotopes can also undergo electron capture (the conversion of a proton to a neutron through the absorption of an electron) to become radon. Francium isotopes with masses of 220 AMU and higher can undergo β-decay (the conversion of a neutron to a proton through the emission of an electron) to become radium. Francium-223 is the most stable isotope and has a half-life of 21.8 minutes.

α-particle: subatomic particle with 2+ charge and mass of 4; a He nucleus

Naturally occurring francium is the product of a side reaction of the decay pathway of actinium. Actinium-227 generally undergoes β-decay to produce thorium-227, but about 1 percent of the actinium emits an α-particle to form francium-223. Francium can be produced in the laboratory via proton bombardment of thorium and during oxygen 18 (O-18) bombardment of heated gold.

Because of its extremely low abundance, short half-life, and high radioactivity, neither francium nor its compounds have economic applications. SEE ALSO Alkali Metals; Curie, Marie Sklodowska; Mendeleev, Dimitri; Radioactivity.

Nathan J. Barrows

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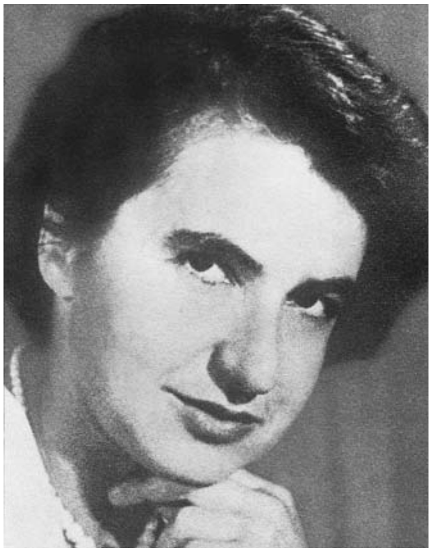
Franklin, Rosalind

ENGLISH MOLECULAR BIOLOGIST
1920–1958

Rosalind Elsie Franklin, the second of four children and the first daughter of Ellis Franklin, a wealthy Jewish banker, and Muriel Franklin (née Waley), was born on July 25, 1920, in London. Although raised in a happy home where children were encouraged to develop their individuality, Rosalind felt discriminated against because she was a girl, a feeling that surfaced again, along with an awareness of anti-Semitism, when she was working on **DNA** at King's College.

DNA: deoxyribonucleic acid—the natural polymer that stores genetic information in the nucleus of a cell



English biophysicist Rosalind Franklin, who made important studies in the structure of DNA.

In 1938 Franklin graduated from St. Paul's Girls' School in London, where, at age fifteen, she decided to become a scientist. Although her father disapproved of college education for women, she attended Newnham College, a women's college at Cambridge University, from which she received a bachelor's degree in 1941. She spent a year (1941–1942) working with future (1967) Nobel chemistry laureate Ronald George Wreyford Norrish, after which she contributed to the World War II effort by working as a physical chemist for the British Coal Utilization Research Association (1942–1945). Her research on the structural changes caused by heating coal resulted in five publications, earned her a doctorate, and made her a recognized authority on crystallography and industrial chemistry.

Franklin's next three years (1947–1950) were spent as a research scientist at the Laboratoire Central des Services Chimiques de l'État in Paris. She became a researcher at King's College, London, in 1951, where she began to work on the structure of deoxyribonucleic acid (DNA), the physical basis of heredity. Her relationship with DNA coworker Maurice Hugh Frederick Wilkins (b. 1916), a biophysicist from New Zealand, soon degenerated into one of mutual dislike. In England two laboratories were working on the crystalline structures of biological materials: King's College was working on DNA, and the Cavendish Laboratory in Cambridge was working on proteins. The American James Dewey Watson (b. 1928) and the Briton Francis Harry Compton Crick (b. 1916) decided that DNA research was more exciting than the protein research in which they were thought to be engaging at the Cavendish.

monoclinic: one of several arrangements of atoms found in crystalline solids; characterized by a unit cell of three axes each of a differing length; two axes are mutually perpendicular while the third is at an oblique angle

Franklin discovered that DNA occurs in two forms (the "A" form, which is more crystalline, contains more water than the "B" form, which is the form that occurs in cells). When Watson and Crick visited King's, Wilkins showed them Franklin's x-ray diffraction photographs of the "B" structure. Her critique of Watson and Crick's earlier work helped them reformulate their structure. However, she failed to recognize the significance of the particular crystal symmetry system (**monoclinic** C2 symmetry) of "B" DNA. Crick, who was working on hemoglobin, which possessed C2 symmetry, recognized that this meant that the strands of nucleic acid are antiparallel, so they could serve as templates for each other. This insight, together with Watson's knowledge of Erwin Chargaff's base pairing, led to their final success. Watson, Crick, and Wilkins received the Nobel Prize in physiology or medicine in 1962.

Watson and Crick wished to publish quickly, before Linus Pauling, but were embarrassed that all the experimental work had been performed at King's, and Franklin's data had not been published. The heads of King's and the Cavendish approached the editors of *Nature*, who agreed to publish three articles in a single issue (April 25, 1953).

Watson and Crick's short paper was followed by an analysis by Wilkins, A. R. Stokes, and H. R. Wilson of the x-ray crystallographic data and Franklin and her graduate student Raymond G. Gosling's conclusion that the phosphate backbone of DNA lies on the outside of the structure. The Watson and Crick paper provided the experimental evidence for the helical structure of nucleic acids. Actually, Franklin and Gosling's paper provided the basis for Watson and Crick's structure, rather than being a confirmation of it.

Because Franklin and Wilkins were hardly speaking to each other, Franklin left King's College in 1953 for Birkbeck College, also in London, where she finished her DNA work and became head of the team studying tobacco mosaic virus. Franklin died of ovarian cancer on April 16, 1958, at the age of 37. SEE ALSO DEOXYRIBONUCLEIC ACID (DNA); DOUBLE HELIX; PAULING, LINUS; WATSON, JAMES DEWEY.

George B. Kauffman

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Freons

The trademark Freon refers to any of several gaseous chlorofluorocarbons, CFCs, with the general formula CF_xCl_{4-x} or $C_2F_xCl_{6-x}$. Due to their physical and chemical properties, these CFCs became the compounds of choice as propellants and refrigerants, substituting for the toxic and flammable sulfur dioxide and ammonia materials used until the early 1930s. Due to their long life, Freons drift for years in the atmosphere and eventually find their way to the stratosphere where they decompose and destroy the protective ozone layer. Current legislation calls for the elimination of Freons.

It was at an American Chemical Society (ACS) meeting in 1930 that Thomas Midgley Jr., of General Motors, announced the synthesis of dichlorofluoromethane by the "Swarts process"—a simple and inexpensive technique named after Belgian chemist Frédéric Swarts who worked on fluorine chemistry in the 1890s (Midgley and Henne, 1930, pp. 542–545). Seeking to make two points, Midgley inhaled the vapors and blew out a candle, thus demonstrating that dichlorofluoromethane was neither toxic nor flammable. The E. I. du Pont de Nemours & Co., working with the Frigidaire Division of General Electric in a joint research program called Kinetic Chemicals, registered these CFCs under the trademark of Freons.

Du Pont introduced a system of naming the CFCs according to the numbers of fluorine, hydrogen, and carbon atoms they contain. The number farthest to the right is the number of fluorines; the second digit from the right is the number of hydrogens plus one; and the third digit from the right is the number of carbons minus one. Thus, $CHClF_2$ is Freon 22; CCl_2F_2 is Freon 12; CCl_3F is Freon 11 (the zero, for the number of carbons, does not show); $C_2Cl_2\ F_4$ is Freon 114; and Freon 113 is $C_2Cl_3F_3$.

Freons are essentially colorless, odorless, nonflammable, and nontoxic. Their low boiling points, low surface tension, low viscosity, insolubility in water, and general chemical inertness are quite remarkable: They remain stable in hot concentrated mineral acids and are unaffected by molten sodium. These properties result from the strong C–F bonds that become shorter as the fluorine atom to carbon atom ratio increases. Thus, the C–F bond length is 1.39 Å (angstroms) in CH_3F, 1.358 Å in CF_2Cl_2, 1.332 Å in CHF_3, and 1.323 Å in CF_4.

Because of their inert properties, Freons were quickly employed as ideal fire extinguishing, cleansing, and foaming agents, as solvents, and as aerosol propellants. Their low-pressure properties allow them to vaporize easily, and thus they were used as refrigerants. While their chemical inertness makes them valuable, it also creates a problem, as they persist in the environment for long periods, eventually diffusing into the stratosphere (altitudes of 25–40 kilometers; 15–25 miles) to decompose and then destroy the protective layer of ozone. This ozone is essential to human and animal life because it absorbs the Sun's ultraviolet light. Without this protection, blindness, genetic damage, and skin cancers can result.

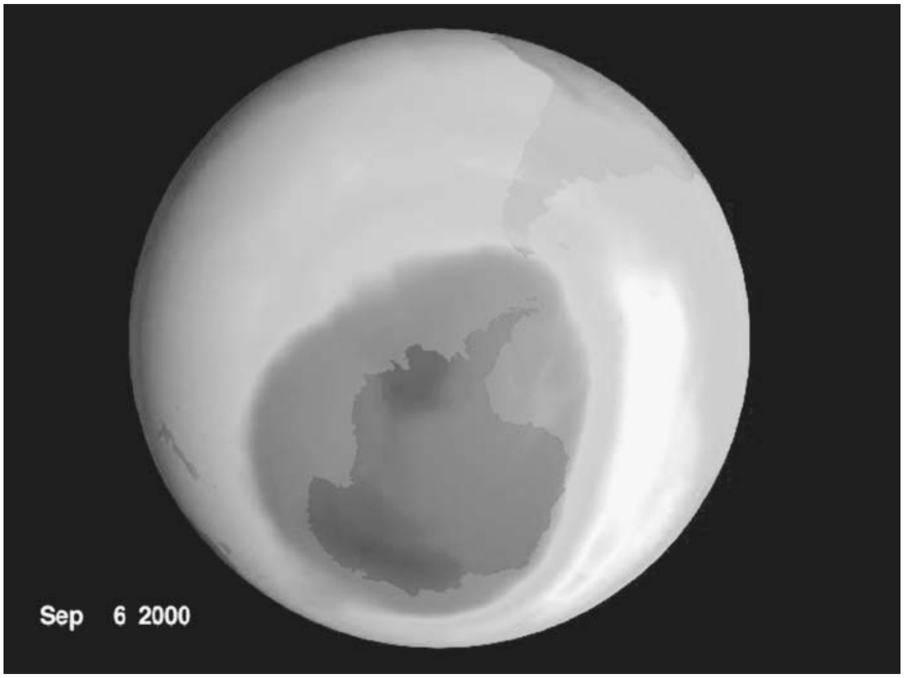
In the mid-1970s F. Sherwood Rowland and M. Molina showed evidence that Freons might drift freely and remain unaffected for up to 100 years, eventually move to the ozone layer, produce free chlorine atoms, and possibly destroy ozone (Molina and Rowland, 1974, pp. 810–812). They thus laid the foundation for a theory of ozone depletion and, together with Paul Crutzen of the Max Planck Institute, received the Nobel Prize for chemistry in 1995. In 1985 Joseph C. Farman, et al. published an article demonstrating the large volume of diminished ozone over Antarctica (Farman, Gardiner, and Shanklin, 1985, pp. 207–210).

In the stratosphere Freons decompose with exposure to ultraviolet light

$$CCl_2F_2(g) + \text{uv light} \rightarrow CF_2Cl(g) + Cl(g)$$

and the chlorine atoms destroy ozone

$$Cl(g) + O_3(g) \rightarrow ClO(g) + O_2(g)\ O(g) + ClO(g)$$
$$\rightarrow Cl(g) + O_2(g)\ O(g) + O_3(g) \rightarrow 2\ O_2(g)$$



The decomposition of Freons in the atmosphere contributes to the destruction of the ozone layer. In this image, the ozone hole is visible over Antarctica.

The oxygen atom is formed in a separate reaction through the light-induced destruction of oxygen molecules.

$$O_2 + \text{uv light} \rightarrow 2\ O$$

It has been estimated that one chlorine atom has an atmospheric lifetime of one to two years and may destroy 100,000 ozone molecules, thus contributing to the mysterious "ozone hole." The British Antarctic Survey discovered the lowest ozone concentration in Earth's atmosphere ever recorded, in October 1984: nearly 40 percent less than the historical average for Antarctica. Atmospheric currents concentrate CFCs over Antarctica, creating the ozone hole that in 1984 was larger than the United States and taller than Mount Everest. The loss of ozone as a protective layer permits the penetration of increased levels of ultraviolet light to Earth's surface.

Today Freons are banned by an international agreement, and substitutes are sought. The United States has banned the production of CFCs since 1977. Non-ozone-depleting alternatives include hydrofluorocarbons (HFCs) and hydrochlorofluorocarbons (HCFCs) such as CH_2FCF_3 (HFC 134a) and $CHCl_2CF_3$ (HCFC 123). In 1987 an international treaty, the Montreal Protocol, called for reducing CFCs, and a 1992 amendment to the treaty called for an end to CFC production. By 1993 CFC emissions had dropped dramatically. A total of 148 countries have now signed the Montreal Protocol calling for HCFCs to be phased out by 2020 and replaced by HFCs, which contain no chlorine and have a short lifetime. The black market of CFCs is of such proportion that *Scientific American* has reported (Beardsley, 1998, p. 32) that "the illegal CFC trade is one of the greatest threats to ozone-layer recovery." SEE ALSO Organic Halogen Compounds; Ozone.

Erwin Boschmann

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Fuels ***See Coal; Energy Sources and Production; Fire, Fuels, Powerplants; Gasoline; Petroleum.***

Fullerenes

inert: incapable of reacting with another substance

In 1985, while working in the laboratory of Richard Smalley at Rice University, graduate students Jim Heath and Sean O'Brien found that carbon aggregates in an **inert** atmosphere form C_{60} (and to a lesser extent, C_{70}) as the most abundant species. Previous work in the Smalley laboratory had involved clusters of atoms such as silicon, germanium, and gallium arsenide. The primary motive was to find out how elements like silicon contrive to minimize their "dangling bonds" on the surface of a small, nanoscopic bare cluster composed of only 10 to 100 atoms. Dangling bonds are ones found on the edges of the cluster that do not have the full complement of electrons that would be provided by bonding to other atoms. These workers had found that some silicon clusters adopt particularly stable structures, but never become so inert that they will not readily react with another silicon atom.

In the case of carbon, the specific cluster C_{60} was clearly behaving as if it had absolutely no dangling bonds as other carbon clusters continued to grow to even larger sizes in the condensing carbon vapor. Somehow the cluster had arranged in geometrical form to eliminate all dangling bonds. The only reasonable structure was a spherical one—a soccer ball—in which each carbon atom had the full complement of electrons. This epic-making work was published in the scientific journal *Nature* in 1985; senior investigators Richard E. Smalley, Robert F. Curl, and Harold W. Kroto were awarded the Nobel Prize in 1996.

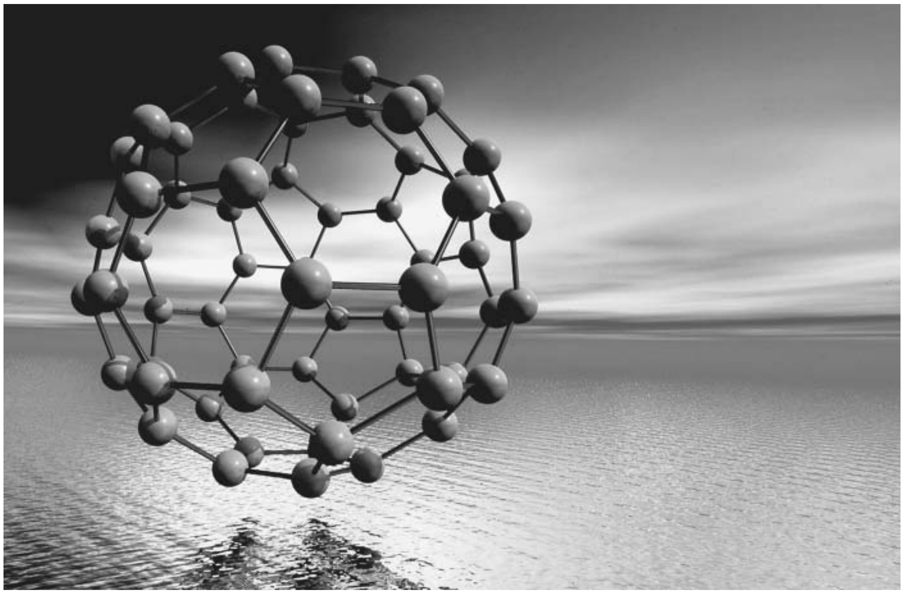

Figure 1. A computer graphic of a buckyball molecule, or carbon cluster, also called a Buckminsterfullerene, named after American engineer Buckminster Fuller.

As stated by Smalley, "the name [fullerene] was born in the dimmest early thinking of how a pure carbon cluster of 60 atoms could eliminate its dangling bonds" (Billups and Ciufolini, 1993, foreword vi). In an effort to make clear the shape of the cluster, Smalley asked Kroto the name of the architect who worked with big domes. The answer was Buckminister Fuller. Carbon clusters of all sizes were subsequently named Buckminsterfullerenes, fullerenes, or sometimes "buckyballs." A third allotrope of carbon had thus been added to the two (graphite and diamond) already known (see Figure 1).

Fullerenes were available initially only in vanishingly small quantities in the gas **phase**. An important breakthrough came in 1990 when Wolfgang Kratschmer of the Max Planck Institute for Nuclear Physics and Donald Huffman of the University of Arizona found that fullerenes could be synthesized in gram quantities by electric arc discharge between graphite electrodes immersed in a **noble gas**. The fullerenes C_{60} and C_{70} can be isolated readily from the crude soot along with several larger fullerenes. With an abundant supply of these fascinating new materials at hand, a flurry of activity directed at establishing a preliminary picture of fullerene chemistry ensued. The literature is now replete with descriptions of fullerenes that have been isolated using many of the **reagents** that are available to the organic chemist.

phase: homogeneous state of matter

noble gas: element characterized by inert nature; located in the rightmost column in the Periodic Table

reagent: chemical used to cause a specific chemical reaction

Fullerenes with **metals** trapped inside their cage may be formed when a graphite target is **doped** with the metal so that the fullerene grows around the metal. Chemists at Yale University have found that helium can be introduced by heating the fullerene under a high pressure of helium. In this way, a window is formed in the fullerene, which closes as the mixture is cooled, trapping the helium inside the fullerene. The **endohedral** fullerenes containing metals are promising candidates as magnetic resonance imaging agents.

metal: element or other substance the solid phase of which is characterized by high thermal and electrical conductivities

dope: to add a controlled amount of an impurity to a very pure sample of a substance, which can radically change the properties of a substance

endohedral: descriptive term for a point within a three-dimensional figure

Carbon nanotubes are fullerene structures played out as long strands rather than spheres. In 1993 Sumio Ajima working at the NEC Corporation in Japan discovered that carbon nanotubes could be created using a process similar to the one used by Kratschmer and Huffman to synthesize

C_{60}. These nanometer-scale structures became the focus of enormous interest since they represent potential building blocks for nanostructured materials, composites, and novel electronic devices of greatly reduced size.

catalyst: substance that aids in a reaction while retaining its own chemical identity

Single-wall carbon nanotubes (SWNTs) can be prepared by laser-vaporization of a graphite source. A newer process uses carbon monoxide as the source of the carbon and is called the HiPco process. The **catalyst** is generated in situ from iron carbonyl. The SWNTs from the HiPco process are characterized by a smaller diameter and exhibit greater reactivity with organic reagents.

Since nanotubes are basically rolled-up sheets of graphite, many different tubes with different diameters and structures can be formed. Even a minor difference in the structure of the nanotube can make the material act like a metal or a semiconductor. Semiconducting nanotubes fluoresce upon exposure to light by emitting the light at a different wavelength. Since nanotubes fluoresce differently depending on their structure, it is possible to find an optical signal for each type of tube. In this way, a team of scientists at Rice University have identified thirty-three semiconducting varieties that are formed in the HiPco process, emphasizing the difficulty that researchers face as they attempt to carry out research with these materials. Nevertheless, carbon nanotubes hold great promise as precursors for strong fibers, electrical conductivity of copper and thermal conductivity of diamond, and perhaps even a means of perfecting deoxyribonucleic acid (DNA). SEE ALSO Allotropes; Carbon; Nanochemistry.

W. E. Billups

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Fusion ***See Transmutation.***

Gadolin, Johan

FINNISH CHEMIST
1760–1852

lanthanides: a family of elements (atomic number 57 through 70) from lanthanum to lutetium having from 1 to 14 4f electrons

Johan Gadolin became an expert in the chemistry of the elements known as the **lanthanide** series of elements. From 1775 to 1779 he studied mathematics, then chemistry, in Åbo, Finland. From 1779 to 1782 he studied chemistry in Uppsala, Sweden. He received a master of science degree at the age of twenty-two, in 1782. During his Uppsala years he became friends with the Swedish chemists Carl Wilhelm Scheele (1742–1786) and Johan Gottlieb Gahn (1745–1818).

In 1786 he undertook a "grand tour" of Denmark, Germany, Holland, England, and Ireland. In Germany he met Lorenz Crell (1744–1816), the editor of the journal *Chemische Annalen.* They became friends, and it was in Crell's journal that many of Gadolin's research papers were eventually published in an international forum. In Ireland Gadolin worked with the Irish chemists Adair Crawford (1748–1795) and Richard Kirwan (1733–1812), investigating specific heat capacities and specific latent heats. After his return to Finland, Gadolin continued to his work in this area.

Gadolin is recognized for having discovered the element yttrium in 1794. He had been studying a black mineral that had been found by Karl Axel Arrhenius (1757–1824) in Ytterby, Sweden. The mineral was eventually named gadolinite. Working with the mineral, Gadolin was able to isolate an oxide substance (apparently the oxide of a new element) that was later named yttria. The existence of the new element, yttrium, was eventually confirmed.

In 1880 the French chemist Jean-Charles-Galissard de Marignac (1817–1894) studied samples of erbium **metal** that had been extracted from gadolinite. He discovered that the erbium metal contained minute amounts of a second metal. He named the metal (and the element) gadolinium, after the mineral.

metal: element or other substance the solid phase of which is characterized by high thermal and electrical conductivities

From 1785 to 1822 Gadolin was a professor of chemistry at the university in Åbo (formerly the Academy of Turku). He believed that students should learn chemistry by working in a laboratory and he enunciated that belief. Because the laboratory at the university was unsatisfactory, he built his own and invited his students to work there.

Gadolin added to the university's reputation, and when offered a chair at the university of Göttingen in Germany, he declined. Gadolin took part in the collective life of his motherland. Johan Gadolin is part of the Finnish national identity. SEE ALSO Erbium; Gadolinium; Lanthanides; Minerals; Scheele, Carl; Yttrium.

Ole Bostrup

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rare earth elements: older name for the lanthanide series of elements, from lanthanum to lutetium

lanthanides: a family of elements (atomic number 57 through 70) from lanthanum to lutetium having from 1 to 14 4f electrons

Gadolinium

MELTING POINT: 1,311°C
BOILING POINT: 3,233.0 °C
DENSITY: 7.89 g cm^{-3}
MOST COMMON ION: Gd^{3+}

64
Gd
GADOLINIUM
157.25

Gadolinium is a chemical element. Its ground state electronic configuration is $[Xe]4f^7 5d6s^2$. Monazite and bastnasite are the principal gadolinium ores, in which gadolinium occurs together with other members of the **rare earth elements** or the **lanthanides**. It can be separated from the other rare earths by ion exchange or solvent extraction techniques. Gadolinia, the oxide of gadolinium, was first extracted from the mineral gadolinite by Jean-Charles-Galissard de Marignac in 1880. (Gadolinite is named after the Finnish chemist Johan Gadolin.) In 1886 Paul-Émile Lecoq de Boisbaudran independently separated the oxide of gadolinium from Carl Mosander's "yttria" (impure yttrium oxide).

Gadolinium is a silver-white, malleable, and **ductile metal**. Gadolinium metal is ferromagnetic just below room temperature. Gadolinium chemistry is dominated by the trivalent gadolinium(III) ion, Gd^{3+}. This ion forms ionic bonds with **ligands** containing an oxygen or nitrogen donor atom. The ground state electronic configuration of Gd^{3+} is $[Xe]4f^7$. In **spectroscopic**

ductile: property of a substance that permits it to be drawn into wires

metal: element or other substance the solid phase of which is characterized by high thermal and electrical conductivities

ligand: molecule or ion capable of donating one or more electron pairs to a Lewis acid

spectroscopy: use of electromagnetic radiation to analyze the chemical composition of materials

Gadolinium yttrium garnets are used in microwave devices, such as this oven.

analysis there are no absorption bands in the visible region of the electromagnetic spectrum, and gadolinium compounds are colorless.

reagent: chemical used to cause a specific chemical reaction

nuclear: having to do with the nucleus of an atom

Gadolinium(III) chelates are used as contrast **reagents** in magnetic resonance imaging (MRI). Due to the high magnetic moment of the paramagnetic Gd^{3+} ion (with its seven unpaired electrons), the relaxation time of water molecules in the proximity of Gd^{3+} ions is greatly reduced and signal intensity is thereby enhanced. MRI is a medical diagnostic technique that depends on the proton **nuclear** magnetic resonance (NMR) signal from water in its creation of a proton density map. Gadolinium is a major component of x-ray phosphors, such as $Gd_2O_2S{:}Tb^{3+}$, within which it dilutes the active emitter (Tb^{3+}) to avoid concentration quenching. Because gadolinium effectively absorbs neutrons, this element has found some use in control rods for nuclear reactors. SEE ALSO Cerium; Dysprosium; Erbium; Europium; Gadolin, Johan; Holmium; Lanthanides; Lanthanum; Lutetium; Neodymium; Praseodymium; Promethium; Samarium; Terbium; Ytterbium.

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31
Ga
GALLIUM
69.72

Gallium

MELTING POINT: **29.78°C**
BOILING POINT: **2,250°C**
DENSITY: **5.907 g/cm^3**
MOST COMMON IONS: **Ga^{2+}, Ga^{3+}**

In 1870 Dimitri Mendeleev predicted many of the properties of an unknown element that he called eka-aluminum. The element was discovered in 1875 by Paul-Émile Lecoq de Boisbaudran who named it gallium from Gaul, the Latin name for France. The properties of the new element were those predicted by Mendeleev and helped to validate his Periodic Table of the elements.

Gallium can be obtained as a by-product of zinc and alumina production. The **metal** has an unusually low melting point but a very high boiling point. The liquid range is the largest known for any element, allowing gallium to be used in high-temperature thermometers. The liquid metal has a number of unusual properties: It has a tendency to supercool; to expand on **crystallization**; and does not crystallize in any of the common closely packed or body-centered cubic structures.

The chemistry of gallium is very similar to that of aluminum, its **congener**. Compounds of gallium almost always have a +3 **oxidation** state. While a few compounds with a +1 and +2 state have been postulated, these are controversial.

metal: element or other substance the solid phase of which is characterized by high thermal and electrical conductivities

crystallization: process of producing crystals of a substance when a saturated solution in an appropriate solvent is either cooled or some solvent removed by evaporation

congener: an element or compound belonging to the same class

oxidation: process that involves the loss of electrons (or the addition of an oxygen atom)

One of the most important uses of gallium is in electronic devices, usually in the form of gallium arsenide, which, together with other group-3 or group-5 elements, converts electrical energy to light, and is the basis of the light-emitting diode.

Metallic gallium and its salts have little or no toxicity, compared to the very toxic thallium salts. The toxicity of the aluminum ion is controversial. The gallium ion has been investigated as a possible antitumor agent, but no clinically useful compounds have been produced. SEE ALSO INORGANIC CHEMISTRY; MENDELEEV, DIMITRI; SEMICONDUCTORS.

Gus J. Palenik

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Gamma Rays ***See Radioactivity.***

Gardening

A successful garden represents a broad spectrum of chemical processes. Photosynthesis provides the route by which diverse chemical transformations use sunlight, water, carbon dioxide, and inorganic chemical elements to produce life-sustaining organic molecules and oxygen (Equation 1). This solar-powered rearrangement of matter is the foundation of almost all ecosystems and is an important example of how chemistry applies to the study of life.

$$6CO_2 + 12H_2O + \text{light energy} + \text{chlorophyll molecule} \rightarrow C_6H_{12}O_6 + 6\,H_2O + 6\,O_2 \quad (1)$$

Process of photosynthesis

The light reactions that occur in the chloroplasts, in addition to catalyzing the evolution of oxygen, also produce ATP and NADPH. ATP energy drives the endergonic reactions, and NADPH drives the reducing power required to bind the hydrogen ions to carbon atoms, and thus to synthesize all the organic compounds necessary for the growth and development of plants in a garden. Plants retrieve the needed ATP energy and reducing power by stripping away the energetic electrons and using them to make the high-energy compound ATP. This is possible because the electrons still carry the energy contributed by their encounter with the **photon** of light. When electrons are removed from chemical bonds, the food molecules are oxidized (i.e., lose electrons). Under **aerobic** conditions, the electrons that are harvested (as ATP is being formed) are eventually donated to oxygen gas, in a process known as cellular respiration (Equation 2).

photon: a quantum of electromagnetic energy

aerobic: involving oxygen or requiring it

$$C_6H_{12}O_6 + 6\ O_2 \rightarrow 6\ CO_2 + 6\ H_2O + \text{energy (heat or ATP)} \qquad (2)$$

Aerobic (cellular) respiration

Plants (including algae) are uniquely self-sufficient in that they are able to harvest and transform radiant energy into the chemical energy required to transform chemically simple molecules and elements (CO_2, H_2O, and nutrient elements) into substances (including carbohydrates, fats, proteins, alcohols, and hormones) needed for the garden plants to complete their life cycle, and to produce harvestable products.

Chemical processes that occur in the soil and aerial environment determine the extent and rate of all plant metabolic processes. The crop growth factors—water, light, essential nutrient elements (Table 1), temperature, and space—are utilized most efficiently when the chemical, physical, and microbiological interactions among the crops, soil, and air are optimal.

Almost all physiological processes in plants take place in the presence of water. Essential anabolic reactions (photosynthesis, assimilation, and protein synthesis), and catabolic ones (respiration and hydrolysis) occur in an aqueous cellular environment. Essential elements absorbed by plant roots, and the foods and other metabolites manufactured by the leaves and other tissues, move in aqueous solution from the regions of absorption or manufacture to other parts of the plant where additional **anabolic** reactions and ultimate food storage take place. Water is the major constituent of protoplasm, and is particularly abundant in young and growing tissues.

anabolic: characteristic of a reaction that builds complex molecules from simpler ones and requires energy

Good soil quality is essential for the crop's root system to function properly, and to ensure that all added chemicals are used efficiently. Incorporating into the soil the required amounts of lime (for soil pH adjustment) and fertilizer (all nutrients needed to amend the soil) is an important first step toward improving soil quality and creating a suitable rooting environment for crops. Deep placement of phosphorus in the soil is beneficial for several reasons. This element is sparingly soluble in the water present in the soil, especially when the soil is cold and/or when the soil pH is not properly adjusted (see Figure 1), and therefore phosphorus diffuses slowly to the site of uptake by roots. Phosphorus is the first essential mineral element the newly growing seedling requires from soil after the seed reserves (phytic acid) for this element are exhausted.

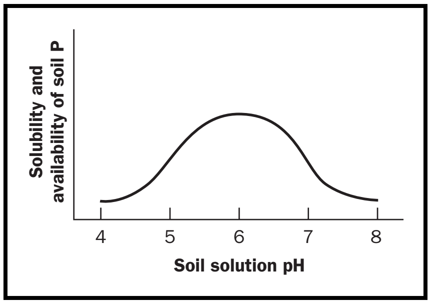

Figure 1. Solubility/availability of soil solution phosphorus as a function of soil pH. The relationship shown is for soil low in organic matter. As organic matter in the soil increases, the curve shifts to the left.

A healthy root system functions to absorb water and dissolved chemicals and translocate them to the above-ground tissues. Many crop growth regulators, hormones, and other chemicals crucial to providing biotic and

Table 1.

ELEMENTS ESSENTIAL[A] FOR CROP GROWTH, AND THE FORM MOST COMMONLY ABSORBED[B]

	Mostly from Air and Water	Mostly from Soil Solids/Fertilizer
Macronutrients[c]	Carbon (CO_2)	Nitrogen (NO_3^-, NH_4^+)
	Hydrogen (H_2O)	Phosphorus ($H_2PO_4^-$, HPO_4^{2-})
	Oxygen (O_2, H_2O)	Potassium (K^+)
		Calcium (Ca^{2+})
		Magnesium (Mg^{2+})
		Sulfur (SO_4^{2-})
Micronutrients[d]		Boron (BO_3^-)
		Chlorine (Cl^-)
		Cobalt (Co^{2+})
		Copper (Cu^{2+})
		Iron (Fe^{2+})
		Manganese (Mn^{2+})
		Molybdenum (MoO_4^{2-})
		Nickel (Ni^{2+})
		Zinc (Zn^{2+})

[a] Essential means that 1) without this element the plant cannot complete its life cycle (i.e., produce a viable seed), and 2) no other element may substitute for the element in question.
[b] Most readily absorbed form (i.e., most soluble in soil solution at suitable soil pH) in parentheses.
[c] Used in relatively large amounts (>0.1% of dry plant tissue).
[d] Used in relatively small amounts (<0.10% of dry plant tissue).

abiotic stress tolerance to the crop are synthesized in roots. Many of these chemical substances are translocated from root to shoot tissues in the same part of the vascular system (xylem tissue) as is the water, dissolved nutrient elements, and soil-applied pesticides. Some of the root-synthesized organic chemicals (such as the hormone abscisic acid) have a profound impact on the structure and function of above-ground tissues (leaf and reproductive tissue abscission and stomatal control of gaseous exchange, for example).

A healthy root system also will secrete organic chemicals (such as sugars, organic acids, and amino acids) into a cylindrical soil zone around the root system that is relatively rich in heterotrophic soil organisms. These soil microbes use these chemicals as energy and carbon sources for their own growth and reproduction, and catalyze many soil chemical transformations that are vital to the garden. With suitable soil moisture, temperature, and aeration, and in the presence of the appropriate microbes, a portion of the immobilized N, P, and S is converted to the inorganic form, and thus becomes available for plant uptake. Many of the essential elements cycle between organic and inorganic forms continuously throughout the growing season.

The key to ensuring that garden soil is in a proper chemical condition is to make certain that the soil pH and nutrient element status are correct for the crops of interest. Each crop has one pH value at which it grows best. Normally, the higher the amount of organic matter in the soil, the lower is the ideal soil pH.

Soil acidity commonly is decreased by supplying carbonates, oxides, or hydroxides of calcium and magnesium, compounds that are referred to as agricultural limes. Wood ashes (as from a fireplace) also are used to help raise soil pH. The primary sources of carbonates, and by far the most commonly used of all liming materials, are calcite, mostly $CaCO_3$, and dolomite, primarily $[CaMg(CO_3)_2]$. Given the fact that the balance of nutrients in plant tissues (the balance of N-P-K-Ca-Mg-S, for example) is even more important than the absolute amount of each nutrient present. Dolomite usually is the preferred liming material, because it supplies relatively equivalent quantities of two essential nutrients. Other sources of carbonates, such as marl, oyster shells, basic slag, and precipitated carbohydrates, all of which are relatively slow-acting, are also used to help control acidity.

Two additional sources of lime are noteworthy, especially when a rapid change in soil pH is desired. Calcium oxide (CaO), called quicklime or burned lime, and calcium hydroxide $[Ca(OH)_2]$, called hydrated lime, are more irritating to handle, and more expensive, than is limestone, but are sometimes favored by gardeners who desire to adjust soil pH quickly.

All liming materials, whether oxide, hydroxide, or carbonate, react with soil water and carbon dioxide to yield the bicarbonate form when applied to acid soil. The partial pressure of carbon dioxide in the soil usually is several hundred times greater than that in atmospheric air, and drives the reaction that produces $Ca(HCO_3)_2$, which is very important in buffering the soil solution (see Equation 3).

$$CaCO_3 + H_2O + CO_2 \rightarrow Ca(HCO_3)_2 \tag{3}$$

Reaction of lime with carbon dioxide

Two attributes are required of any liming material: 1) a cation capable of displacing soil colloid-adsorbed H^+ and Al^{+++}(also a source of soil acidity); and 2) an anion capable of neutralizing the displaced H^+ and Al^{+++} (see Equation 4).

$$\text{Soil colloid } -H^+ \text{ \& } Al^{+++} + 2CaCO_3 + H_2O \rightarrow \text{Soil colloid}—2Ca^{2+} + Al(OH)_3 + 2CO_2 \tag{4}$$

Reaction of lime with soil colloids

The insolubility of $Al(OH)_3$ and the diffusion of CO_2 to the atmosphere drive this reaction to completion. Also, adsorption of cations onto the colloid complex raises the percentage base saturation (extent to which the colloidal complex is saturated with exchangeable cations other than hydrogen and aluminum, expressed as a percentage of the total cation exchange capacity) of the colloidal complex, increasing the pH of the soil solution accordingly.

Soil with an appropriate pH for the crops being grown will provide the essential nutrient elements in the most soluble form, and also will retain these elements in the effective rooting zone most fully, because the nutrients are more likely to be chemically adsorbed on the colloidal exchange complex, and less subject to leaching loss. One major problem resulting from raising the soil pH above about pH 6.5–6.7 is that several of the essential micronutrient elements begin to precipitate out of solution, becoming unavailable for uptake. Soils high in clay and/or organic matter are much harder to overlime, and generally require a slightly lower pH for optimal crop growth.

The vast majority of crops normally grown in most gardens are healthiest when the mineral soil pH is inthe 5.8–6.2 range. These crops grow equally well in soils fairly high in organic matter (2-5%) at a somewhat lower pH, in the 5.2–5.6 range.

The color of the blooms on the hydrangea plant, which can be pink, blue, or purple, are determined by the amount of acidity in the soil.

The decomposition of organic matter in the soil, and the reaction of NH_4^+-containing fertilizer materials in soil solution, contribute to an increase in soil acidity, especially when the soil is well-aerated and warm, and when the right kinds of bacteria are present (Equation 5). The process begins with the microbially-induced mineralization of nitrogen from organic to the NH_4^+ form, followed by a two-step nitrification process. In the first step, obligate autotrophic bacteria (*Nitrosomonas spp.*), that obtain their energy from the oxidation of nitrogen and their carbon from CO_2, oxidize NH_4^+ to NO_2^-. In the second reaction, NO_2^- is further oxidized to NO_3^- in the presence of autotrophic bacteria (*Nitrobacter spp.*). Under certain conditions other bacteria can be involved in both nitrification steps. The reaction rates associated with nitrification in most well-drained soils are NO_2^- to $NO_3^- > NH_4^+$ to NO_2^-. As a result, NO_2^- generally does not accumulate in soils, which is fortunate, because this ion is toxic to plant roots. The nitrate ion is more mobile than is the ammonium ion, and therefore much more highly leachable. Factors promoting nitrification in soils include 1) supply of ammonium, 2) population of nitrifying organisms, 3) soil pH, 4) soil aeration, 5) soil moisture, and 6) temperature. Because nitrification is suppressed in a cold soil, ammonium-containing fertilizers applied in the late fall or winter promote accumulation of ammonium rather than nitrate, and thus nitrogen is retained in the garden soil rather than being lost through leaching. Under wet soil conditions, and in the presence of anaerobic bacteria, the nitrate ion can be lost through denitrification to N_2, NO_x and N_2O, which is a greenhouse gas, and thus potentially a contributor to global warming (see Equation 5).

$$\text{Organic matter} \xrightarrow{\textit{Mineralization}} 2NH_4^+ + 3O_2 \xrightarrow{\textit{Nitrosomonas spp.}} 2NO_2^- + 2H_2O + 4H^+ \; 2NO_2^- + O_2 \xrightarrow{\textit{Nitrobacter spp.}} 2NO_3^- \quad (5)$$

One of the greatest values of a properly limed and pH-adjusted soil is that applied fertilizer and pesticide materials are much more likely to remain in

A soil tilth test using compost.

the soil. This practice leads to the retention of more fertilizer elements in the effective rooting zone during periods of heavy rain. A higher proportion of a properly-limed soil colloid's cation exchange capacity is comprised of basic ions, such as calcium and magnesium, rather than hydrogen ions, thus reducing the potential for leaching loss of essential elements. Considering the relative strength of cation adsorption on the surface of soil colloids (both inorganic and organic), hydrogen ions are held the strongest, followed by aluminum, calcium, magnesium, potassium/ammonium, and finally sodium ions (held least tightly). The more fully the cation exchange capacity of a soil is satisfied by calcium and/or magnesium (i.e., the better limed it is), the lower is the leaching potential of applied nutrient elements such as potassium.

Another important reason for maintaining soil pH at the proper level is that most of the soil microorganisms that benefit the garden in so many ways (for example, decaying plant residues that otherwise would serve as a haven for pathogens and insects) function best in a well-limed soil. The bacteria that are able to produce nodules (tumor-like growths on the roots that serve as the site for symbiotic biological nitrogen fixation) on the roots of legume crops, for example, function best at pH 6.3-6.5. When the legume crop is healthy, and the proper strains of symbiotic bacteria are present (each legume requires its own bacterial strains), the nitrogenase enzyme (provided by the bacteria) within the nodule catalyzes the reduction of diatomic nitrogen gas to the ammonium form of nitrogen, one of the two forms of nitrogen (nitrate being the other) plants can readily use. Since the heterotrophic bacteria obtain their required energy (of ATP) from the host plant, this association is a true symbiosis. The legume plant dedicates about 14-18 moles of ATP for each mole of nitrogen gas reduced. When a legume crop is planted, and when this symbiotic relationship is functioning properly, no synthetic nitrogen fertilizer needs to be applied, and subsequent nonlegume crops planted in the same area will benefit from the residual nitrogen ultimately returned to the soil from the legume crop's residues.

A healthy garden represents a chemical laboratory in which a host of chemical processes are occurring in synchrony with our natural world. When the gardener has chosen adapted crop varieties, and has managed both soil and crops wisely, these chemical processes unfold in such a way that the garden harvests the sun's energy efficiently, and converts a portion into useful products. SEE ALSO AGRICULTURAL CHEMISTRY; HERBICIDES; INSECTICIDES; PESTICIDES.

Robert P. Patterson
Donald E. Moreland

Gases

A gas is a state of matter in which a substance does not have a specific shape or volume of its own, but adopts the form and size of its container. It was the early-seventeenth-century Flemish chemist-physician Jan Baptista van Helmont who coined the word "gas" (from the Greek *chaos*) in order to convey the idea that a gas had an indefinite shape and size. This is an apt name because, as was later hypothesized and confirmed, gas molecules are distributed uniformly throughout a container without any apparent spatial organization, and they undergo incessant, seemingly chaotic, random motion.

A liquid, like a gas, has no shape of its own, but it does have a definite volume. Both states of matter are referred to as fluids because of their mobility, or tendency to flow. A gas is actually a low density fluid because the molecules are much farther apart than in a liquid where molecules are in close contact with each other. For example, at room temperature and at atmospheric pressure the density of air is about 0.0012 grams (0.000042 ounces) per cubic centimeter (g/cm^3), whereas the density of liquid air is approximately 0.810 g/cm^3 (at its normal boiling point of -209°C, or -344°F). This corresponds to an average separation between molecules in the gas **phase** that is about nine times larger than that for the liquid. A liquid is thus called a condensed phase—or a high density fluid—and is roughly 1,000 times more dense than a gas.

phase: homogeneous state of matter

A compound exists in the gaseous state because the attractive forces between the molecules are weak and/or the average distance between them is large. Liquifaction, or condensation of the gas, may occur if the kinetic energy of the molecules is reduced (by cooling) and/or the intermolecular distance is made smaller (by compression).

Gas Properties

There are four intrinsic, measurable properties of a gas (or, for that matter, any substance): its pressure P, temperature T, volume (in the case of a gas, the container volume) V, and mass m, or mole number n. The **gas density** d is a derived quantity, which is m/V. Before the relationships between these properties for a gas are discussed, the units in which they are usually reported will be outlined.

gas density: weight in grams of a liter of gas

Pressure is defined as force per unit area. In the International System of Units (SI, or mks), unit pressure corresponds to one newton per square meter, which is denoted as one pascal or Pa (named after Blaise Pascal, the seventeenth-century French scientist). There are several other, more commonly used pressure units, however. One is the atmosphere or atm; it is based on the magnitude of the pressure actually exerted by Earth's atmosphere at sea level. Because atmospheric pressure varies, one atmosphere is simply defined as the pressure that is exerted by a 760-mm-high column of mercury, a dense liquid sometimes used to measure pressures. Note that 760 mm is equivalent to 29.91 inches, which is close to the value sometimes cited in weather reports of atmospheric pressure. Another pressure unit is the torr (named after the seventeenth-century Italian scientist Evangelista Torricelli). One torr is equivalent to one mm Hg.

One pascal corresponds to a very small pressure as compared with one atm, that is, $1\ \text{Pa} = 9.86923 \times 10^{-6}$ atm. The bar is another commonly used pressure unit. One bar is defined as 10^5 Pa and is equal to 750 torr.

Temperature is often reported in degrees Celsius. One Celsius degree is defined as 1/100 of the temperature difference between boiling water and freezing water (both at 1 atm pressure). In this scale, the temperature of pure water at its freezing point is 0°C (32°F) at 1 atm pressure. Another important temperature scale is the *absolute temperature*. The absolute temperature of pure liquid water in coexistence with ice and water vapor (the triple point) is defined as exactly 273.16 kelvins (K). This condition corresponds to 0.01°C, and thus the relationship between the Celsius *(t)* and Kelvin scales *(T)* is

$$t = T - 273.15^\circ$$

The significance of the Kelvin scale is that 0 K represents the lowest temperature that can, in theory, be attained and corresponds to the condition in which molecular translational and rotational motion ceases.

The SI unit of volume is the cubic meter (m^3), but in most scientific applications, volumes are usually measured in cubic centimeters (cm^3) or liters (L). One liter contains 1,000 milliliters (mL), or equivalently, 1,000 cm^3.

The SI unit of quantity is called the mole (symbol n and abbreviation mol). It is derived from the Latin *moles* (meaning "a mass"). One mole of a substance contains Avogadro's number of elementary units of the substance. Because atoms and molecules are extremely small entities, Avogadro's number (N_A) is incomprehensibly large, 6.022×10^{23} particles/mol. Thus, one mole of hydrogen atoms contains 6.022×10^{23} H atoms, one mole of sucrose molecules consists of 6.022×10^{23} sucrose molecules, and so forth.

Relationships among Gas Properties

From the earliest days of quantitative inquiry, scientists have sought to uncover the mathematical relationships that describe natural phenomena, including the properties of gases. Because there are four fundamental properties of a gas, namely, P, T, V, and n, discovering the relationship between any two requires that the other two properties be kept constant. Some of the earliest quantitative studies of gases were reported in the mid-1600s by British chemist Robert Boyle, who found that for a fixed amount of a gas at a specific temperature (i.e., constant n and T), the volume was inversely proportional to the applied pressure. This V-P relationship, known as Boyle's law, is represented as

$$V = c/P$$

or

$$PV = c$$

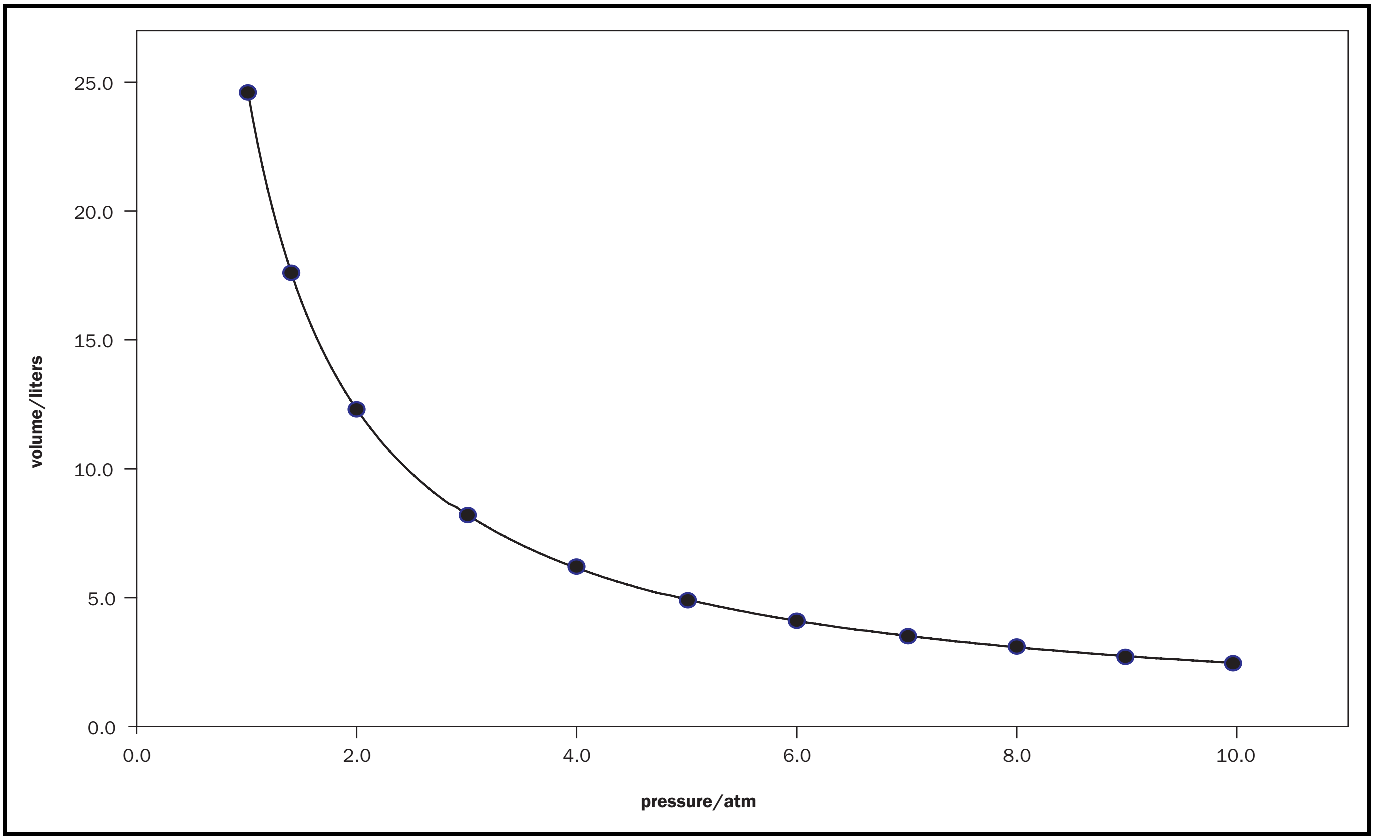

Figure 1. Illustration of Boyle's law. Plot of the volume, in liters, of 1.00 mole of an ideal gas at 300 K versus pressure, in atmospheres.

where c is an experimental constant that depends on the amount of gas and its temperature.

Figure 1 illustrates Boyle's law with a plot of the volume occupied by one mole of a gas at 300 K as a function of pressure.

In the later part of the eighteenth century, French chemist Jacques Charles studied the relationship between the volume of a fixed amount of gas and its temperature, while keeping the gas at constant pressure. He found that V was a linear function of the temperature. Figure 2 graphically represents this relationship, known as Charles's law, with a plot of the gas volume versus the temperature in Celsius, t.

Mathematically, Charles's law is expressed as

$$V = a + bt$$

where a and b are constants. The same data are plotted with expanded scales in Figure 3 to illustrate the fact that the x-intercept a has a value of $-273.15°C$, and it is evident that this value, called absolute zero, corresponds to the temperature at which the volume of a gas extrapolates to zero, its logically limiting value. This condition is the basis of the absolute temperature, or Kelvin scale, and was proposed in the mid-1800s by Lord Kelvin (British physicist William Thomson). Charles's law can be expressed in terms of the absolute temperature as

$$V = c'T$$

where c′ is a constant; thus, the volume of a gas is directly proportional to its absolute temperature.

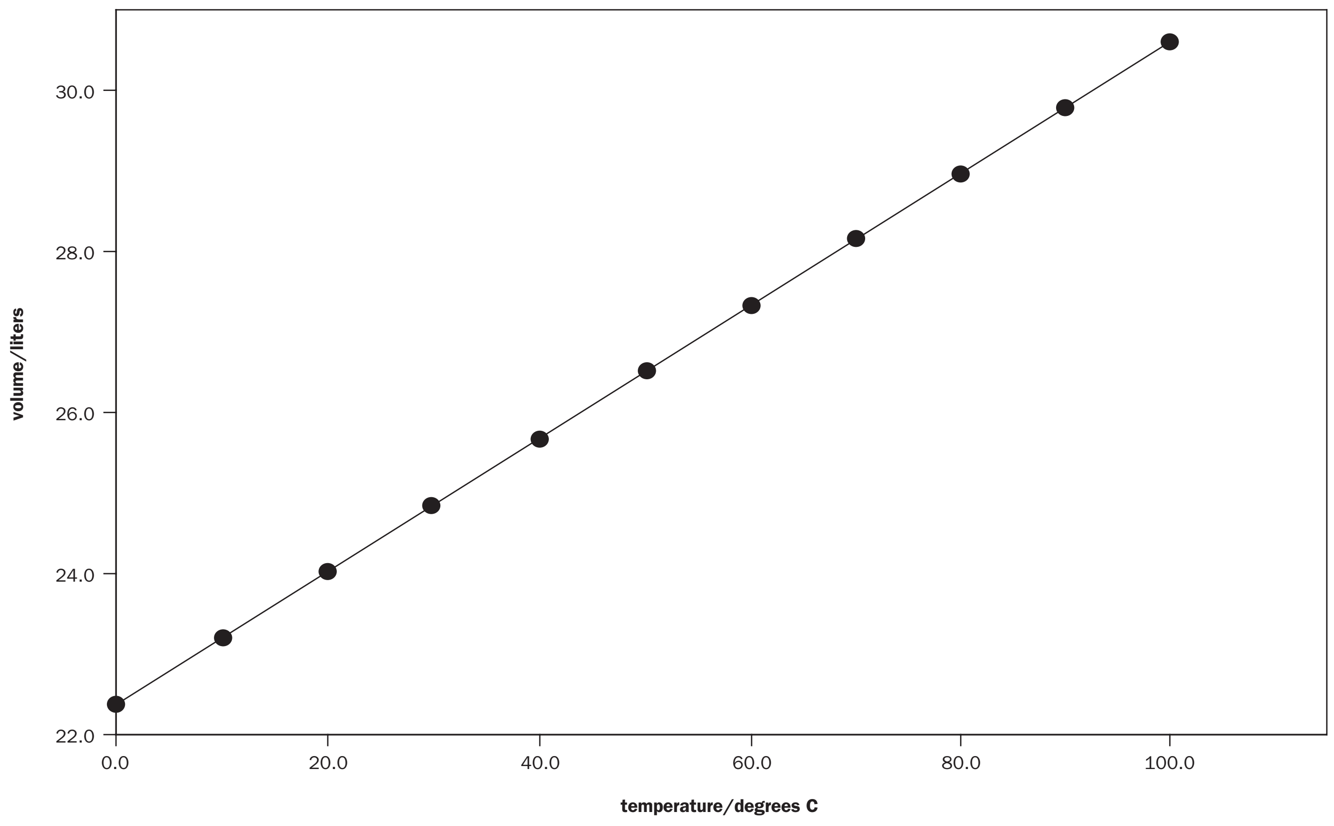

Figure 2. Illustration of Charles's law. Plot of the volume, in liters, of 1.00 mole of an ideal gas at 1.00 atm pressure versus temperature in degrees celsius.

The relationship between the volume of a gas and the quantity of the gaseous material, as represented by the number of moles, was established by Amedeo Avogadro in the early 1800s. He deduced from experiments performed by Joseph-Louis Gay-Lussac that equal volumes of different gases at the same temperature and pressure contained the same number of moles. This idea leads to Avogadro's law, which states that the volume of a gas at constant temperature and pressure is directly proportional to the number of moles of the gas, or

$$V = c''n$$

where c′′ is a constant.

The three relations, Boyle's, Charles's, and Avogadro's laws, connecting the volume of a gas with its pressure, (absolute) temperature, and mole number, respectively, can be combined into one expression, called the ideal-gas equation of state, or $V = nRT/P$, in which R is a universal constant, valid for all gases. The value of R is 0.08206 L-atm/mol-K or, in SI units, 8.314 J/mol-K. The ideal-gas equation is usually expressed as

$$PV = nRT$$

A gas that obeys this equation is called an ideal or perfect gas. Notice that the identity of the gas is not represented in this equation; in this sense, an ideal gas is hypothetical. The ideal-gas equation works well in the limit of low pressures (where intermolecular interactions are negligible) and/or high temperatures.

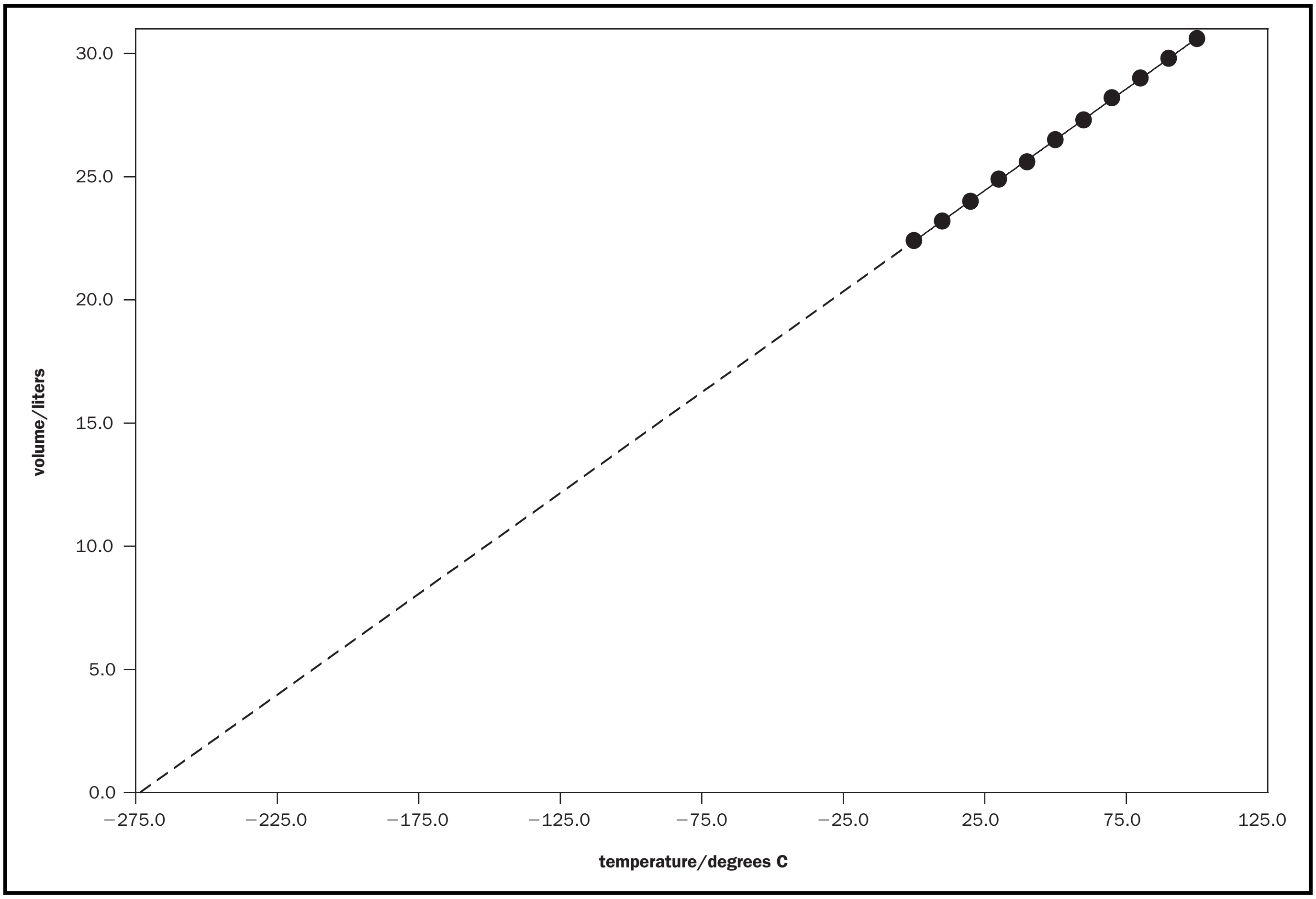

Figure 3. Plot of the data in Figure 2 showing the linear extrapolation to zero volume. The value of the x-intercept is −273.15°C.

There are many other equations of state, such as the van der Waals equation, that are designed to account for gas properties at higher pressures and/or lower temperatures. These equations contain one or more parameters whose values are specific for the gas in question.

Molecular Motion

Beginning with the empirical development of the gas laws, which explained how gases behave, scientists began to seek an understanding of the mechanism of this behavior. By the mid-1800s the work of several scientists, including James Joule, Rudolf Clausius, James Clerk Maxwell, and Ludwig Boltzmann, led to the development of the kinetic-molecular theory (KMT) of gases. This theory employed several assumptions: (1) Gas particles (i.e., atoms or molecules) are point masses—meaning they have negligible volume, (2) they undergo constant random motion involving frequent collisions, (3) attractive and **repulsive forces** between molecules are negligible, and (4) the average kinetic energy of molecules is proportional to the absolute temperature.

repulsive force: force that repels two bodies; charges of the same sign repel each other

According to this model, pressure is caused by the collisions that molecules make with the walls of its container. An analysis of this molecular motion using Newton's laws leads to an expression identical to the ideal-gas law. An important result of the theory is that the average kinetic energy of one mole of gas can be expressed in terms of the absolute temperature

Table 1. Composition of gases in Earth's atmosphere at sea level in volume (or mole) percent.

COMPOSITION OF GASES IN EARTH'S ATMOSPHERE AT SEA LEVEL IN VOLUME (OR MOLE) PERCENT

Component	Composition (% by Volume)[a]
N_2, nitrogen	78.084
O_2, oxygen	20.948
Ar, argon	0.934
CO_2, carbon dioxide	0.0345
Ne, neon	0.00182
He, helium	0.000524
CH_4, methane	0.000168
Kr, krypton	0.000114
H_2, hydrogen	0.00005
Xe, xenon	0.0000087

[a] Note that percent by volume is equivalent to percent by moles (Avogadro's law)

$$\frac{1}{2}Mu^2 = \frac{3}{2}RT$$

where M is the molar mass, u its average molecular speed, R the gas constant. The average kinetic energy of a gas depends only on T and is independent of its mass. The root-mean-square speed, u_{rms}, of a gas is equal to

$$u_{\mathrm{rms}} = \sqrt{\frac{3RT}{M}}$$

and the KMT predicts that for methane, CH_4 ($M = 0.0160$ kg/mol), near room temperature (300 K) $u_{rms} = 394$ m/s (or 882 miles/hr!). Although this result seems very large, experimental measurements are consistent with this value. Another property obtained from the KMT is the mean free path λ, which is the average distance a molecule travels between collisions. Analysis shows that λ varies inversely with pressure, as well as the size of the molecule, a property not accounted for in simple KMT. For a pure gas,

$$\lambda = \frac{RT}{\sqrt{2}N_A d^2 P}$$

where d is the molecular diameter. For the oxygen molecule O_2, $d \approx 2.4 \times 10^{-10}$m, and $\lambda \approx 1.6 \times 10^{-7}$m at 300 K and 1 atm. Under these conditions, the molecule travels a distance that is about 670 times its diameter before it collides with another molecule.

Earth's Atmosphere

Perhaps the most important and ubiquitous gas is Earth's atmosphere, which is a complex mixture of compounds. The composition of gases in the atmosphere at sea level, excluding water vapor, aerosols, and particulate suspensions, which vary regionally and climatically, is listed in Table 1.

Although carbon dioxide (CO_2) is present in trace amounts, it is an exceedingly important constituent. Until about 1800 CO_2 composition was constant at about 0.028 percent. After that time it began to increase, presumably because of the **combustion** of fossil fuels. In 1900 the CO_2 level was ca. 0.0295 percent; currently it is 0.0345 percent. CO_2 and several other

combustion: burning, the reaction with oxygen

gases, such as methane (CH_4) and nitrogen oxides, which are, in part, anthropogenic, are called greenhouse gases because they absorb infrared radiation from Earth that would otherwise be transmitted into space. Thus, these gases, while transmitting visible light from the Sun, essentially retain heat in a way similar to the glass panels of a greenhouse. The apparent trend in global warming has been attributed to the rapid and continuing increase in the atmospheric composition of greenhouse gases observed in the past 50 to 100 years. SEE ALSO Avogadro, Amedeo; Air Pollution; Boltzmann, Ludwig; Boyle, Robert; Charles, Jacques; Gay-Lussac, Joseph-Louis; Maxwell, James Clerk; Noble Gases.

Arthur M. Halpern

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Gasoline

In 1859 Edwin Drake and E. B. Bowditch of the Seneca Oil Company drilled the first commercial oil well in the United States in Titusville, Pennsylvania. The well produced about 400 gallons of crude oil, less than ten barrels a day. Soon, similar wells all over western Pennsylvania were providing crude oil for kerosene production that was needed to fuel the nation's streetlights and house lamps. The lighter boiling component, gasoline, was discarded, since it had no market. There are historical reports that "waste" gasoline, which had been dumped into rivers, sometimes caught fire. In 1892 the first gasoline-powered engines, for both car and tractor, were developed: This soon provided a market for the once useless substance, gasoline.

Today gasoline is the most important product of a typical oil refinery: The entire refinery process is designed to maximize its production. Gasoline is a complex mixture of molecules with a boiling range of 40–200°C (104–392°F). To produce various grades, there is a blending of many refinery components, each of which promotes specific fuel qualities such as desired octane rating, volatility, and minimization of engine deposits.

Octane Quality

The most important quality parameter for gasoline is the octane quality. Octane number is a measure of the antiknock properties of the fuel. Knocking in a gasoline engine is a metallic clattering noise (pinging), which indicates excessive intensity in preflame reactions. Severe knocking can damage the engine.

Preflame reactions occur in the engine cylinders when portions of the fuel self-initiate **combustion** prior to the advancing flame from the spark plug. This additional combustion causes an excessive rate of energy release, which is knock. The tendency of a fuel to engage in preflame reactions is dependent upon the structure of its component molecules (see Figure 1);

combustion: burning, the reaction with oxygen

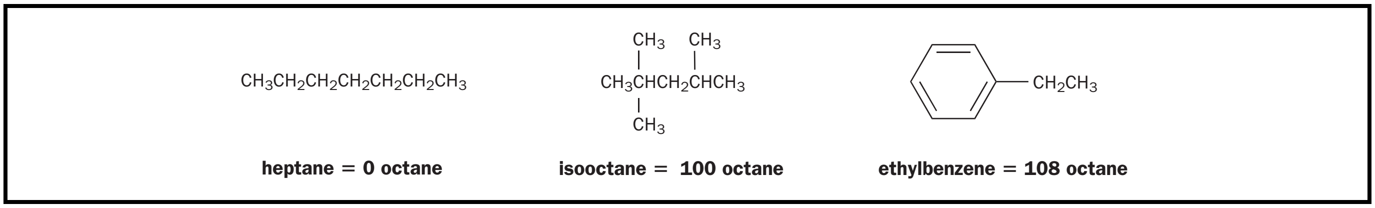


Figure 1. The tendency of a fuel to engage in preflame reactions depends on the structure of its component molecules.

the tendency for preflame reactions is high for straight chain hydrocarbons, medium for branched hydrocarbons, and low for aromatics.

The octane number for a test gasoline represents the percentage by volume of isooctane (2,2,4-trimethylpentane) in a reference fuel consisting of the mixture of isooctane and heptane that would be necessary to match the test fuel's knocking tendency. Isooctane burns with a minimal knocking and is given an octane rating of 100. This is in contrast to heptane, which burns with much knocking and is given an octane rating of 0. Thus, a gasoline that burns with the same amount of knocking as a mixture of 92 percent isooctane and 8 percent heptane is classified as a 92 octane gasoline.

The octane ratings of gasoline can be increased by the addition of small amounts of antiknock agents. The first commercially successful antiknock agent, tetraethyllead (TEL), was developed in the 1920s. TEL was used to promote the development of higher efficiency, higher compression engines. However, TEL is highly toxic and poisons **catalytic** converters. Since 1974 all new U.S. automobile engines have used catalytic converters in order to reduce exhaust emissions.

catalysis: the action or effect of a substance in increasing the rate of a reaction without itself being consumed.

Methyl *t*-butyl ether (MTBE) has been the antiknock agent of choice for unleaded gasoline. MTBE provides high-octane quality along with low volatility and is readily soluble in gasoline. However, leakage of gasoline from underground storage tanks has resulted in the detection of MTBE in the drinking water of several urban areas. This prompted the state of California to order the removal of MTBE from California gasoline by 2003.

Alcohols also have found use as octane enhancers. At higher concentration alcohols can be used as gasoline extenders, thus decreasing our dependency upon imported crude oil. A significant portion of all U.S. marketed gasoline is believed to contain ethanol.

Gasoline Additives

Trace amounts of olefins and diolefins found in gasoline are prone to reaction with oxygen dissolved in the gasoline. This process is referred to as autoxidation and involves a radical chain reaction that can incorporate oxygen

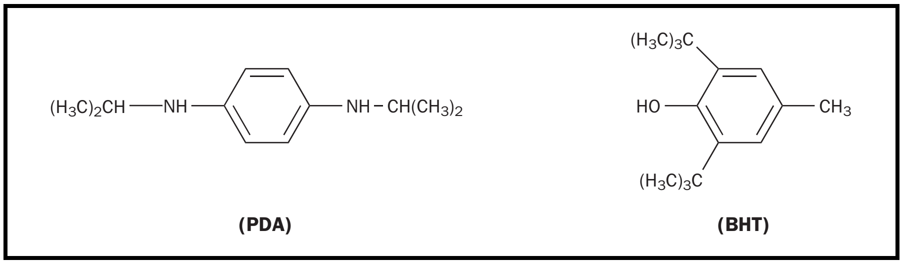


Figure 2. The chemical structures of the two different types of antioxidants used in gasoline are phenylenediamines (PDA) and hindered phenols (such as BHT).

into the olefin and also can promote a molecular size increase via polymerization reactions. The end result of this complex process is the formation of deposits and gums that can block fuel filters and interfere with the metering of fuel and air in the carburetor. This can result in adverse engine performance. Additives are frequently added to gasoline to address oxidative stability and other issues; they include antioxidants, **metal** deactivators, and detergents.

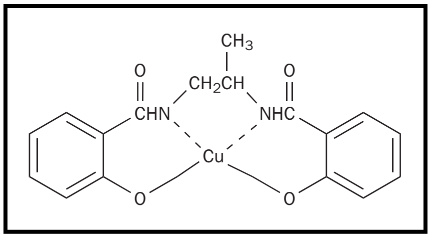


Figure 3. Structure of the copper complex of the most widely used metal deactivator N, N′-disalicylidene-1,2-propanediamine.

Antioxidants are additives that minimize autoxidation reactions. They function as hydrogen atom donors that stop the chain oxidation process of the olefins. The two different types of antioxidants used in gasoline are phenylenediamines (PDA) and hindered phenols (such as BHT).

Trace levels of soluble metal compounds, particularly copper, catalyze the oxidative degradation of gasoline by promoting the formation of gums and deposits. Metal deactivators overcome this problem by chelating the metal and rendering it inactive. The most widely used metal deactivator is N, N′-disalicylidene-1,2-propanediamine, the copper complex of which is shown in Figure 3.

metal: element or other substance the solid phase of which is characterized by high thermal and electrical conductivities

Detergents minimize fuel system deposits at low concentrations, and at high concentrations can remove deposits that have already formed. Detergents are molecules that have a highly polar end group and a **nonpolar** hydrocarbon tail. A conventional amino amide type detergent is shown in Figure 4.

nonpolar: molecule, or portion of a molecule, that does not have a permanent, electric dipole

Presumably, the polar groups in the detergent attach themselves to metal surfaces and to polar deposits on these surfaces. The nonpolar tails of these molecules "stick out" into the fuel in such a way that a monomolecular film is formed on the metal surface, preventing deposition and particle aggregation. This process is also believed to solubilize any deposits already on the metal surface. The detergent monolayer is also believed to prevent the build-up of ice on carburetor surfaces during winter. Thus, detergents can also function as anti-icing additives.

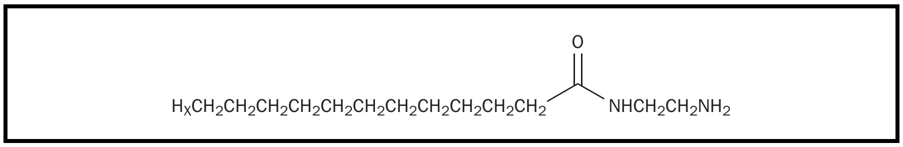
Gasoline Production

The production of gasoline begins with desalting the viscous crude oil. Salts and metals in the crude oil promote corrosion and poison processing catalysts. Thus, the crude oil is heated (to decrease viscosity) and extracted with water to remove the salts and metals. Frequently this process results in the formation of an oil/water mixture referred to as an **emulsion** (suspension). This emulsion is typically broken by the addition of a chemical **surfactant** (demulsifier) that promotes the separation of discrete oil and water layers. After separation of the aqueous layer, the oil is heated to about 400 °C (752°F): This converts the oil into gaseous products and increases the fluidity of the remaining liquid. In this form, the gaseous mixture enters the fractionating column, where the process of atmospheric **fractional distillation** separates the crude oil into different components based upon boiling point.

emulsion: immiscible two-phase mixture in which one phase is dispersed (as small droplets) in the other phase

surfactants: surface-active agents that lower the surface tension of water; e.g., detergents, wetting agents

fractional distillation: separation of liquid mixtures by collecting separately the distillates at certain temperatures



$$H_XCH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2C(=O)NHCH_2CH_2NH_2$$

Figure 4. A conventional amino amide type detergent.

The lightest boiling fractions are molecules that are gases under ambient conditions: methane, ethane, propane, butane, and olefins derived from these compounds. Uses for this distillate stream include burning as a fuel at the refinery; as petrochemical feed stocks; or processing into liquefied petroleum gas (LPG). There are three other major distillate streams collected during atmospheric distillation: the naptha fraction, which has a boiling range of 30 to 180°C (86–356°F); the kerosene fraction, which distills at between 180 and 240°C (356–464°F); and the gas oil fraction, which distills at between 240 and 355°C (464–671°F).

catalyst: substance that aids in a reaction while retaining its own chemical identity

In order to meet current environmental regulations for the sulfur content in fuel products, the three-distillate streams are subjected to the process of hydrodesulfurization. In the presence of a **catalyst**, distillates are heated in the presence of hydrogen to reduce various organosulfur compounds to simple organic compounds and H_2S. The hydrogen needed for this process is a by-product of the catalytic reforming process. The H_2S product can be readily removed. In this process the refiner can control the octane number of the gasoline blending stock. By heating the naphtha fraction in the presence of an especially designed platinum catalyst, straight-chain hydrocarbons are cyclized, and saturated cyclic hydrocarbons are converted into aromatic compounds. In addition, this process converts straight-chain hydrocarbons into branched hydrocarbons. Catalytic reforming facilitates the production of gasoline blending stocks with octane ratings of from 90 to 100+.

Redistilling the atmospheric residue at a temperature of less than 400°C (752°F) under vacuum produces a vacuum gas oil. Typically, the vacuum gas oil is subjected to fluid catalytic cracking (FCC) to produce lower-boiling liquids that can be blended to make gasoline. This is achieved by breaking large molecules of the vacuum gas oil into smaller, lower-boiling molecules. An important gasoline blending component that can be produced in this manner is alkylate. It is a mixture of highly branched hydrocarbons produced by the acid-catalyzed reaction of isobutene and light olefinic hydrocarbons. Alkylate is a valuable blending component because of its high-octane quality and the absence of aromatics or olefins, which can lead to environmental and oxidative stability problems.

The 1990 Clean Air Act required the Environmental Protection Agency (EPA) to issue regulations that required gasoline to be "reformulated," resulting in significant reductions in vehicle emissions of ozone-forming and toxic air pollutants. This cleaner gasoline is called reformulated gasoline (RFG). RFG is required in the nine major metropolitan areas in the United States having the worst ozone problems. In addition, several other areas with ozone levels exceeding the public health standard have voluntarily chosen to use RFG.

volatile: low boiling, readily vaporized

Use of RFG decreases the amounts of **volatile** organic compounds (VOCs) and oxides of nitrogen (NO_x) in the atmosphere that react in the presence of sunlight to produce ozone, a major component of smog. Vehicles also release toxic emissions, one of which (benzene) is a known carcinogen.

RFG contains 2 percent by weight oxygen additives (oxygenates), such as MTBE or ethanol. Oxygenates increase the combustion efficiency of gasoline, reducing vehicle emissions of carbon monoxide, a serious public health threat. The appearance of MTBE in some urban water supplies has resulted in legislation pending in the U.S. Congress to phase out the use of MTBE in RFG. Ethanol would then most likely become the primary oxygenate for future RFG.

Gasoline is the most important product of the oil refinery. The most important quality parameter for gasoline is its octane number. Additional quality characteristics for gasoline are controlled by the use of additives, for example, antioxidants, metal deactivators, and detergents. By blending various refinery streams and additives a gasoline formulation can be achieved that minimizes environmental degradation. Such a fuel is called reformulated gasoline. SEE ALSO DETERGENTS; ENERGY SOURCES AND PRODUCTION; FOSSIL FUELS; PETROLEUM.

Bruce Beaver

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Gay-Lussac, Joseph-Louis

FRENCH CHEMIST AND PHYSICIST
1778–1850

Joseph-Louis Gay-Lussac was one of the great scientists of the industrial age. Born on December 6, 1778, in St. Léonard in central France, he was the eldest of five children. His father was a public prosecutor and judge advocate, and the political unrest surrounding the French Revolution played an early role in young Joseph's development. When his father was arrested in 1794 (he was later released) as a member of the bourgeois establishment, Gay-Lussac was sent to a boarding school in Paris.

Three years later Gay-Lussac was accepted to the newly founded and elite École Polytechnique in Paris, where he initially studied mathematics and engineering. However, he soon fell in love with science and especially chemistry. This was in no small part due to the influence of the renowned scientist Claude-Louis Berthollet (1748–1822), a lecturer at the École who was also a contemporary of Antoine Lavoisier. It was Berthollet who took Gay-Lussac under his wing as his student and laboratory assistant.

The research for which Gay-Lussac is perhaps most famous involves the experiments with gases he completed early in his scientific career. Upon graduation from the École in 1800, he remained Berthollet's assistant and a frequent guest at his country house at Arcueil, near Paris. With the encouragement of Berthollet, mathematician Pierre-Simon de Laplace, and others, Gay-Lussac began his own research in the winter of 1801 and 1802.

Among Gay-Lussac's early work was an extensive investigation of how the volume of various gases changes with temperature. The English scientist John Dalton was independently studying the same phenomenon. Both found that the volume V of all gases studied increased similarly with higher temperature T when pressure P was held constant ($V \alpha T$ at constant P). Each published his results around 1802, with Gay-Lussac's experimental work being both more thorough and more precise than that of Dalton. However,

French chemist and physicist Joseph-Louis Gay-Lussac, who published the "Law of Combining Volumes of Gases."

the credit for this discovery typically goes to neither Dalton nor Gay-Lussac, but instead to Jacques Charles. Charles had done some initial work on the thermal expansion of gases in 1787. Although Charles never published the results of his experiments, in his own scientific memoirs Gay-Lussac acknowledged hearing of Charles's work. Thus, the law governing the thermal expansion of gases, while sometimes called Gay-Lussac's law, has come to be known largely as Charles's law.

Gay-Lussac's studies were not limited to the physical properties of gases. In 1804 Gay-Lussac took advantage of the world's growing interest in ballooning and made multiple flights to study both Earth's magnetic field and how the temperature and composition of the atmosphere changed with increasing altitude. On his second flight, he took samples of air while reaching an altitude of 23,018 feet in a hydrogen balloon, a record that lasted for almost fifty years. Upon his return to Earth, he compared the gas samples to those taken at ground level and concluded that they were essentially identical—this despite making note of a headache during the flight that very possibly resulted from the decreased oxygen levels at high altitude.

In 1808 Gay-Lussac published his "Law of Combining Volumes of Gases." He determined that when different gases reacted, they would always do so in small whole number ratios (e.g., two volumes of hydrogen would react with one volume of oxygen in forming H_2O). This was one of the greatest advancements of its time and helped form the basis for later **atomic theory** and how chemical reactions occur.

atomic theory: concept that asserts that matter is composed of tiny particles called atoms the particular characteristics of which determine the type and form of the matter

With his colleague Louis-Jacques Thénard (1777–1857), Gay-Lussac did considerable work with electrochemistry to produce significant amounts of elemental sodium and potassium, highly reactive and useful substances that were used to isolate and discover the element boron. Gay-Lussac also completed extensive studies of acids and bases and was the first to deduce that there were binary (two element) acids such as hydrochloric acid (HCl) in addition to the known oxygen-containing acids like sulfuric acid (H_2SO_4). Additionally, he was able to determine the chemical composition of prussic acid to be hydrocyanic acid (HCN) and was considered the foremost practitioner of organic analysis.

In later years, Gay-Lussac continued to advance science. He developed a precise method for analyzing the alcoholic content of liquors and patented a method for the manufacture of sulfuric acid. His last publication on aqua regia (a mixture of nitric and hydrochloric acids that dissolves gold or platinum) came out the year before his death in 1850. Gay-Lussac was a top-notch experimentalist and theoretician. More than twenty-five years after Gay-Lussac died, the prominent chemist Marcellin Bertholet (1827–1907) once said, "We all teach . . . the chemistry of Lavoisier and Gay-Lussac" (Crosland, p. 248), a fitting tribute to two outstanding scientists of the era. SEE ALSO Acid-Base Chemistry; Berthollet, Claude-Louis; Charles, Jacques; Dalton, John; Davy, Humphry; Lavoisier, Antoine.

David A. Dobberpuhl

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Gelatin *See Collagen.*

Gemstones

There are several thousand known minerals in nature (with estimates ranging from 2,000 to 7,000), but fewer than a hundred are considered gem minerals. Of these, only about a dozen or so are actually valuable enough to be important gemstones on the world market. In order to be considered a gemstone, a mineral must first of all be beautiful. In addition, it must be hard and durable. Its value increases if it is also rare.

The beauty of a gem is measured in terms of its clarity, brilliance, and color. Its natural beauty can be enhanced by the way it is cut. There are two basic kinds of gem cuts: faceted and cabochon. The faceted cut has many flat cut surfaces (facets) with an overall shape that might be round, oval, square, rectangular, or pear-shaped. Faceted cuts are preferred for brilliant transparent stones such as diamond. The cabochon cut has a smooth rounded top, usually with a flat base, and it is mainly used for opaque or translucent stones.

Hardness is measured using the Mohs' scale, on which 10 is hardest. (Diamond has a hardness of 10.) Gemstones should have a Mohs' hardness of 6 or more. A really durable gem should have a hardness of at least 7, which is the hardness of quartz. Table 1 shows the hardness of some familiar minerals on the Mohs' scale.

The value of a gemstone depends on its beauty and its rarity, but also the size of the stone. Size is measured in terms of weight using the carat as a unit. A carat is 0.2 grams (0.007 ounces). (A 10-carat diamond weighs 2 grams, or 0.07 ounces.) There are 100 points in a carat, so a 30-point diamond weighs 0.3 carat, or 0.06 grams (0.002 ounces). Since gemstones vary in density (weight per unit volume), several different 1-carat stones may vary in size, the stones with the greatest density being smaller than the others.

Some Important Gemstones

Diamond is the hardest substance known to occur in nature, measuring 10 on the Mohs' scale. It is pure carbon in a tightly packed cubic structure. Diamonds are usually graded on the basis of four Cs: carat, cut, clarity, and color. Carat refers to the stone's weight and degree of flawlessness. As for color, diamonds are usually colorless, but sometimes they do exhibit color. The famous Hope diamond, for example, is blue. Most diamonds come from mines in Africa, especially southern Africa, although Russia and Australia also have diamond mines. Industrial-grade diamonds have even been made synthetically at very high pressures and temperatures. A number of other softer colorless stones are often sold as imitation diamonds.

Ruby is a variety of corundum (Al_2O_3) with a Mohs' hardness of 9. Its red color results when chromic ions (Cr^{3+}) replace some of the aluminum ions in the crystal. The finest rubies come from Myanmar (formerly Burma) or Kenya. Star rubies are stones with a special starlike appearance. They usually have a cabochon cut and appear to show a 6-pointed star due to microscopic inclusions. Rubies of very high quality are sometimes made synthetically.

Sapphire, like ruby, is made of corundum (Al_2O_3) and has a hardness of 9. However, instead of Cr impurities, the crystal contains iron and titanium

Table 1.

Mohs' HARDNESS SCALE

Mineral	Chemical Composition	Hardness
Talc	$Mg_3Si_4O_{10}(OH)_2$	1
Gypsum	$CaSO_4$	2
Calcite	$CaCO_3$	3
Fluorite	CaF_2	4
Apatite	$3\ Ca_3(PO_4)_2{\bullet}CaF_2$	5
Feldspar	$K_2Al_2Si_6O_{16}$	6
Quartz	SiO_2	7
Topaz	$Al_2SiO_4F_2$	8
Corundum	Al_2O_3	9
Diamond	C	10

ions, which produce a blue color, ranging from very pale to very dark blue. Sapphires are found in Cambodia and other places in Southeast Asia and Australia, as well as Montana in the United States. Also, as in the case of rubies, there are star sapphires, which exhibit a 6-pointed star. Pure corundum (white sapphire) was the first gem to be produced synthetically. It was a poor substitute for diamond, however, because of its low refractive index. Adding about 0.1 percent chromium, however, produces rubies of excellent quality; and the addition of iron and titanium yields beautiful blue sapphires. Even star sapphires and rubies that rival natural stones can be made synthetically.

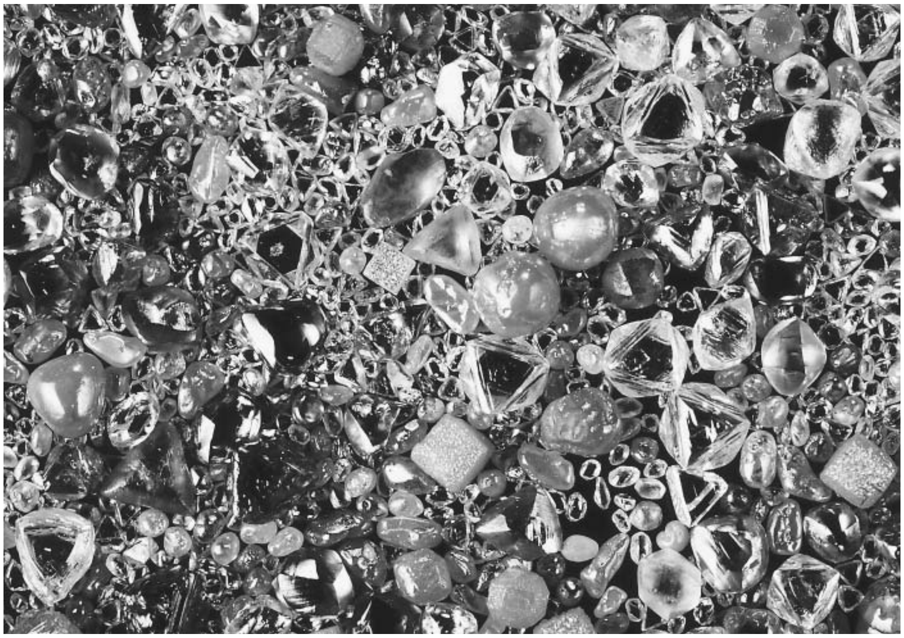
Emerald is a variety of beryl, a beryllium silicate, with a hardness of 7.5 to 8. It has a beautiful deep green color, and it is one of the most expensive gems, sometimes outranking diamond in value. The green color results from small amounts of chromic oxide (Cr_2O_3). The oldest emerald mines were in Egypt near the Red Sea, but the best emerald mines today are in Colombia. There are others in Brazil, Pakistan, and Africa; synthetic emeralds of excellent quality have also been manufactured.

Aquamarine, like emerald, is a transparent variety of beryl, or beryllium silicate. Its light blue to blue-green color results from small amounts of iron in the crystal. Like most beryl stones, it measures 7.5 to 8 on the Mohs' hardness scale. Most aquamarine gemstones come from Brazil.

Topaz is a rather rare silicate mineral with a Mohs' hardness of 8. It comes in many colors from yellow to pink to purple to blue, depending on what ions are present in the crystal. It can even be colorless. However, the favorite variety is orange to brown in color and called "imperial topaz." Much of the best topaz comes from Brazil. The gem called London blue topaz can be made from the colorless variety by treatment with heat and radiation.

Cubic zirconia (ZrO_2), with a Mohs' hardness of 8, is a beautiful, usually colorless, stone that is made synthetically. Although not as hard as diamond, cubic zirconia has much fire and brilliance, and it is popular as an imitation diamond. Zirconia normally has a **monoclinic** crystalline structure at room temperature, but when heated to about 2,300°C (4,172°F), it takes on a cubic structure. Ordinarily, it would revert to the monoclinic structure on cooling, but the addition of yttrium oxide (Y_2O_3) or calcium oxide (CaO)

monoclinic: one of several arrangements of atoms found in crystalline solids; characterized by a unit cell of three axes each of a differing length; two axes are mutually perpendicular while the third is at an oblique angle



A mixture of natural and synthetic diamonds. Diamonds are the hardest natural substance known.

can stabilize the zirconia so that it retains the cubic structure at room temperature. Cubic zirconia has optical properties very close to those of diamond, and it is clearly the best of all the various diamond imitations.

Zircon is native zirconium silicate ($ZrSiO_4$) that exhibits beautiful transparent crystals and a Mohs' hardness of 7.5. The tetragonal crystals are usually brownish yellow in color. Also known as jargon or jargoon, zircon is a stable and durable silicate crystal. Small crystals of zircon are among the oldest mineral grains ever found on Earth.

Opal is a hydrous silica (SiO_2), sometimes thought of as an amorphous silica gel. It is a fairly soft gem, measuring only 5 to 6 on the Mohs' scale. It is relatively common in nature except in its "precious" form, which comes mainly from Australia. In Switzerland, since 1970, opal of precious quality has been made synthetically. Usually cut in the cabochon shape to permit its rainbowlike display of color, opals come in white, black, and fire varieties. "Black" opals are dark gray to blue, and fire opals, which are more transparent than other opals, are usually orange-red in color.

Amethyst is a variety of quartz (SiO_2) that is violet to purple in color, probably because of iron and manganese impurities. It measures 7 on the Mohs' hardness scale and is obtained from many places, but mainly from India and Brazil. It should not be confused with oriental amethyst, which is a purple native variety of alumina (Al_2O_3).

Spinel is a colorless magnesium aluminate ($MgAl_2O_4$) of cubic structure. It is hard and durable, but, like white sapphire, it is not a good diamond substitute because it has a low refractive index and lacks brilliance. However, it is readily **doped** to produce other gems of various colors. Artificial ruby, for example, is often natural red spinel, and most synthetic blue sapphires on the market are actually blue spinel.

dope: to add a controlled amount of an impurity to a very pure sample of a substance, which can radically change the properties of a substance

Peridot is the gem variety of olivine, a magnesium silicate containing iron (about 9 Mg atoms for every Fe atom). Peridot is usually transparent,

A handful of a variety of gemstones. The beauty of gemstones is measured by their clarity, brilliance, and color.

with a color ranging from greenish yellow to brownish green. Much peridot comes from an island in the Red Sea, but it is also found in Myanmar and an Apache reservation in Arizona.

Garnet is actually a group of related silicates containing various amounts of magnesium, calcium, aluminum, iron, manganese, and chromium. Garnets have a hardness of 6.5 to 7.5, depending on their composition, and their color also varies along with their composition. The popular dark red garnets are found in many gem sites in the Czech Republic, but garnets of many colors are also found in other parts of the world, such as India, Tanzania, Russia, and Brazil.

Tourmaline is a highly complicated silicate, with a wide range of compositions and colors. It probably exhibits more colors than any other kind of gemstone. Sometimes there are several different colors in the same crystal. “Watermelon” tourmaline, for example, is green on the outside but red in the middle.

Lapis lazuli is a deep blue gemstone that is a complex copper silicate mineral varying widely in composition. It often contains sparkles of iron pyrite or calcite. The best source is probably Afghanistan. A pale blue variety is found in Chile. Some material sold as lapis lazuli is actually artificially colored jasper from Germany.

Onyx is a striped variety of the common silicate mineral called agate, with alternating black and white bands. It comes mainly from India and South America. Sardonyx is a variety of onyx with brown and white bands.

“Organic” Gems

The aforementioned gemstones, unless they are synthetic, usually occur in underground deposits from which they are mined. However, there are some gems that come from once living material.

Pearls are little spheres of calcium carbonate ($CaCO_3$) that form in mollusks (**invertebrate** shellfish) such as oysters, usually because of some sort of irritation. They are normally white or off-white in color, but they can have bluish or pink tints, and sometimes they are dark gray. Although many pearls form naturally, pearl production has been greatly increased by the "cultured" pearl industry, which raises beds of oysters into which irritants are routinely introduced. The irritants are usually bits of mother-of-pearl, the lining that forms inside oyster shells.

Amber is fossilized tree resin that hardened over millions of years and now is valued as a gem. Baltic amber is thought to be hardened sap from pine trees. It is normally yellow-brown in color, but the shades vary from almost white to almost black. Although sometimes completely clear, amber often contains inclusions of insects or other matter, often considered desirable. Much amber is obtained along the shores of the Baltic Sea, but it is also found along the coasts of Sicily, Romania, and Myanmar.

Coral, like pearls, is calcium carbonate ($CaCO_3$) derived from living matter. It is the outer shells of small marine animals. It occurs in many colors, from white to deep pink and red. The greatest demand is for red coral. The best coral comes from the Mediterranean Sea, along the coasts of Algeria and Tunisia.

Ivory is a bonelike material that comes from the tusks of animals (elephant, walrus, hippopotamus). It has become such a highly prized material that there are unscrupulous poachers who kill these animals in order to steal their tusks. The pale cream color of new ivory becomes darker with age and turns yellow. Ivory is brittle, but it does not peel as do its plastic substitutes.

Jet is actually just a very hard and dense kind of lignite coal. It was probably plant material millions of years ago that has become fossilized and blackened over time. It often comes from northeast England, where it is derived from fossil driftwood buried under the sea. Its primary drawback as a gemstone is that it will burn (since it is basically just highly polished coal). SEE ALSO GLASS; MINERALS.

Doris K. Kolb

AMBER AND ELECTRICITY

Ancient Greeks called amber *elektron.* When they rubbed it with a cloth, it became charged and attracted bits of paper. The word "electricity" derives from the Greek word *elektron.*

invertebrate: category of animal that has no internal skeleton

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Genes

A gene is a unit of genetic information that codes for a single biological function or product. Genes are found on chromosomes and are made up of nucleic acid (deoxyribonucleic acid [**DNA**] for most organisms) and proteins.

DNA: deoxyribonucleic acid—the natural polymer that stores genetic information in the nucleus of a cell

Table 1.

COMPARISON OF GENE NUMBERS AND DNA FROM DIFFERENT SPECIES

Organism	Number of genes	Number of base pairs (millions)
Yeast	5,800	12
Caenorhabditis elegans (worm)	19,099	97
Fruit fly	13,601	116
Arabidopsis (plant)	25,498	115
Human	30,000–40,000	2,700

SOURCE: Bork, Peer, and Copely, Richard (2001). "The Draft Sequence: Filling in the Gaps." *Nature* 409:818–820.

The information is contained in the sequence of the four nucleic acid components much like the way written information is contained in the sequence of letters in a sentence.

helix: form of a spiral or coil such as a corkscrew

DNA is measured in base pairs (bp) since it occurs as a double **helix**. The sum total of all genetic information in an organism is its genome. Different organisms have different sized genomes with different numbers of chromosomes, genes, and base pairs. Table 1 shows the values for several organisms, including the preliminary results for the human genome from the Human Genome Project (HGP) report. One surprising finding of the HGP was that only 30,000 to 40,000 genes were found. The human genome has almost 3 billion base pairs and many different gene products, so scientists were expecting over 100,000 genes. Results from the HGP suggest that about 75 percent of DNA is "nongene." This DNA is often referred to as "junk" or "selfish" DNA, but some portions do have important functions in maintaining the structure of chromosomes.

code: mechanism to convey information on genes and genetic sequence

eukaryotic: relating to organized cells of the type found in animals and plants

Genes "tell" a cell which molecules to synthesize based on the genetic **code** that those genes contain. The amount of code needed varies widely. Genes vary greatly in size, from those that code for small transfer RNA molecules (tRNAs) and have 73 base pairs, to those that code for very large proteins and have 250,000 base pairs (Maulik and Patel, p. 26). A **eukaryotic** gene for a large protein may be much larger than its coding region due to intervening noncoding sequences (introns). Each gene has two or more coding regions (exons) separated by introns. The introns are "cut out" of the genetic information during expression and do not show up in the final gene product. Some genes have as much as 90 percent intron DNA. Sometimes the exons are cut and pasted from the same gene in different ways, creating two or more different gene products issuing from the same gene. This added flexibility opens the door to even more debate about how genes and gene products are controlled. Although each gene codes for one or sometimes a few gene products (due to splicing variations), biological functions often require many genes working together or in sequence. The proper interplay of genes produces healthy cells. Some forms of cancer occur when certain genes, called oncogenes, become uncontrolled. SEE ALSO CHROMOSOME; DOUBLE HELIX; GENETIC ENGINEERING; GENOME; NUCLEIC ACIDS; PROTEINS.

David Speckhard

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Genetic Code ***See Codon.***

Genetic Engineering

Genetic engineering is a discipline represented by the ability to isolate, modify the expression of, or transfer genetic material. Genetic engineering was born in 1973 when Stanley Cohen and Herbert Boyer reported the successful transfer of reptile **DNA** into bacteria. Practical applications quickly followed, and in 1980 Genentech became the first publicly traded genetic engineering company. Genentech's main product was human insulin produced in bacteria. It was marketed for diabetic patients who had developed allergies to the pig or sheep insulin used to treat diabetes. The enthusiastic response from investors led to many new genetic engineering companies. Many of the newest of their products are produced in genetically engineered animals. This practice is called pharming.

DNA: deoxyribonucleic acid—the natural polymer that stores genetic information in the nucleus of a cell

Insulin was just the first of many genetically engineered products. In 1995 there were over 100 genetically engineered therapeutic products approved by the U.S. Food and Drug Administration (FDA) or in clinical trials. They ranged from hormones like insulin and human growth hormone to vaccines, and included many products created to treat serious diseases such as muscular dystrophy, multiple sclerosis, and cancer. Genetic engineering has allowed scientists to explore genetic material in detail. In 2001 the preliminary report of the Human Genome Project was released, containing the nucleotide sequence of nearly all of the human genome (International Human Genome Sequencing Consortium 2001, pp. 860–921; Venter et al. 2001, pp. 1304–1351). A better understanding of human genetic makeup will allow scientists to understand both healthy cells and diseases better. Scientists are predicting that in a few years a patient will receive a DNA scan that will allow a doctor to prescribe medicines that match that patient's genetic makeup. These genetically tailored medicines are expected to be more effective and to have fewer side effects than their predecessors. A new scan technique called "DNA microarray" or "gene chip" is now available. With this technique a scientist or doctor can scan the identity of all the genes that a given tissue or cell is using at any time. This tool will be very powerful in helping to unravel the complex interactions of genes in diseases like cancer. It has already helped to identify the ways in which chemotherapy drugs interact, so that new more effective drug combinations may be developed. The same tool will help scientists to investigate cell growth and development. One important question that can now be asked is: Which genes are turned off or on as a cell ages?

Corn embryos are being removed to be grown in controlled conditions for desired genetic traits at Sungene Technologies Lab, Palo Alto, California.

One of the most exciting branches of therapeutic genetic engineering is human gene therapy. A single defective gene is often the cause of a disease, for example as with cystic fibrosis or sickle cell anemia. Gene therapy would allow doctors to transfer the healthy gene to the patient, and possibly allow replacement or removal of the harmful gene. For the first time doctors could cure genetic defects instead of being able only to treat the symptoms the defects cause. Trials of human gene therapy began in 1994 with some success (Anderson 1995, pp. 124–128), but much remains to be done before gene therapy can be used routinely. In addition, there are important ethical questions having to do with which genes will be identified as defective and which gene replacements will be allowed.

Agriculture is another area in which genetic engineering has become increasingly important. Many genetically engineered products are used in veterinary medicine and to enhance livestock-related production. For example, Bovine Somatotropin is used to increase milk production in dairy cows. It is becoming more common to use genetically engineered crops. Two of the most common examples are genetically engineered corn and beans. A kind of corn called Bt corn is engineered to contain and put to use a gene from a strain of bacteria that produces a **toxin**. This toxin kills insects that attack the corn so that farmers can use less insecticide on the field. Many soybeans are engineered to withstand a particular herbicide. Farmers can apply the herbicide to kill weeds in a planted field without harming the soybeans. All of these innovations have been very successful, but have provoked some concerns about human exposure to the new products, as well as new ecological concerns about "escape" of these genes into the environment. In one case Bt corn that had not been approved for human consumption accidentally made its way into human food products, and in another case the effects of Bt corn pollen on monarch butterflies have been questioned, but no answer is yet forthcoming. Genetically modified animals used to produce nonfoodstuffs such as those produced in pharming, and as laboratory models, are becoming more common. SEE ALSO AGRICULTURAL CHEMISTRY; CHROMOSOME; CLONES; GENOME; RECOMBINANT DNA.

toxin: poisonous substance produced during bacterial growth

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Internet Resources

Human Genome Project. More information is available from <http://www.nhgri.nih.gov/HGP/>.

Genome

An organism's genome is the complete set of genetic instructions, passed from one generation to the next. The genome consists of a set of instructions for building each of the components of a living cell or virus. The information is found in nucleic acids: usually deoxyribonucleic acid (**DNA**), but sometimes ribonucleic acid (RNA).

DNA: deoxyribonucleic acid—the natural polymer that stores genetic information in the nucleus of a cell

Genetic information is organized into units called genes, each of which provides instructions to build one cellular component. Genes are parts of large strands of DNA called chromosomes. Much of what we know about human chromosomes comes from the Human Genome Project, begun in 1990. In February 2001 David Baltimore of the International Human Genome Sequencing Consortium and J. Craig Venter of Celera Genomics separately announced initial results on the complete sequencing of human DNA. More information about this project is available online. Scientists were able to determine the chemical **code** of chromosomes by applying recombinant DNA techniques, whereby millions of copies of human DNA were reproduced in bacteria, and polymerase chain reaction (PCR), which copies small sections of DNA for sequencing, to amplify a few strands of human DNA into more than a trillion strands, enough to detect in the sequencers. Enough DNA was produced to enable determination of the genetic code. Recombinant DNA also provides the basis for the construction of transgenic species such as Bt corn, which contains a gene from the bacteria *Bacillus thuringiensis* that ultimately helps to protect the corn plant from insects. The terms "biotechnology" and "genomics" are used to describe the application of these new techniques and new genetic information to produce new products. Examples of new biotech products include medical

code: mechanism to convey information on genes and genetic sequence products such as cloned human insulin, human growth factor, and human clotting factors. These products are used to treat diseases caused by genetic errors. The new cloned materials are cheaper and safer than animal substitutes or isolated human materials. Another new biotech product is the herbicide-resistant soybean. These plants allow farmers to kill weeds in fields already planted with soybeans, without affecting the growth of soybeans. SEE ALSO AGRICULTURAL CHEMISTRY; CHROMOSOME; GENES; NUCLEIC ACIDS; POLYMERASE CHAIN REACTION (PCR); RECOMBINANT DNA.

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Internet Resources

Human Genome Project. More information is available from <http://www.nhgri.nih.gov/HGP/>.

32
Ge
GERMANIUM
72.61

Germanium

MELTING POINT: **937.4°C**
BOILING POINT: **2,830°C**
DENSITY: **5.323 g/cm^3**
MOST COMMON ION: **Ge^{4+} Ge^{2+}**

trace element: element occurring only in a minute amount

volatile: low boiling, readily vaporized

tetrachloride: term that implies a molecule has four chlorine atoms present

Germanium has chemical and physical properties similar to those of silicon. It was predicted as an element ("eka-silicon") by Dimitri Mendeleev in 1871 from calculations made during the construction of his periodic table, and it was discovered by Clemens Winkler in 1886. It is 10,000 times less abundant than silicon, and it occurs as a **trace element** in silicate minerals (1–2 ppm). The element is usually obtained via the acid leaching of mineral dusts, especially certain coals and zinc ores (using H_2SO_4) formed during ceramic processing, followed by addition of hydrochloric acid, to form the **volatile** germanium **tetrachloride** ($GeCl_4$), which is easily separated from coprecipitated zinc compounds. Its low abundance and complicated processing make germanium an expensive material: Although some of its semiconducting properties are superior to those of silicon, its use in the electronics industry is limited. Like silicon, germanium forms gaseous hydrides (e.g., GeH_4) and volatile halides (e.g., GeF_4 and $GeCl_4$).

valence: combining capacity

isostructural: for minerals, relating to an arrangement of atomic constituents that is geometrically the same although different atoms are present

Germanium is more reactive than silicon, and the chemistry of its 2+ **valence** state is better developed: Binary solids such as GeF_2 and $GeCl_2$ are known, in addition to the tetrahalides. The monoxide GeO (a dark brown solid) occurs, although the dioxide, GeO_2, is more stable. Germanium dioxide has octahedrally coordinated germanium atoms; the tetrahedrally coordinated quartz phase is stable only at high temperature, although it exists metastably at ambient conditions. This contrasts with SiO_2: The corresponding octahedrally coordinated compound **isostructural** with the mineral **rutile** (TiO_2) form is prepared only at high pressure (>90,000 atmospheres). High pressure treatment of germanium nitride, Ge_3N_4, gives (as with like treatment of silicon nitride) a new high-density form with the same structure as the mineral **spinel** ($MgAl_2O_4$), containing octahedrally coordinated (GeN_6) groups. Like silicon, germanium forms "Zintl" phases with electropositive **metals** (e.g., KGe, $BaGe_2$) that contain unusual polyanions with Ge in negative **oxidation** states, and "semiconductor clathrates" (e.g., Na_8Ge_{44}; $Na_{16}Cs_8Ge_{136}$) with open framework structures constructed from Ge atoms in tetrahedral coordination that are structurally analogous with H_2O-ice clathrates, and with alkali or alkaline earth atoms occupying "cages" in the structure. SEE ALSO MENDELEEV, DIMITRI; SILICON.

Paul F. McMillan

rutile: common name of TiO_2; also a common structural type for compounds with the general composition AB_2

spinel: name given to a group of minerals that are double oxides of divalent and trivalent metals, for example, $MgO \cdot Al_2O_3$ or $MgAl_2O_4$; this mineral is called spinel; also a structural type

metal: element or other substance the solid phase of which is characterized by high thermal and electrical conductivities

oxidation: process that involves the loss of electrons (or the addition of an oxygen atom)

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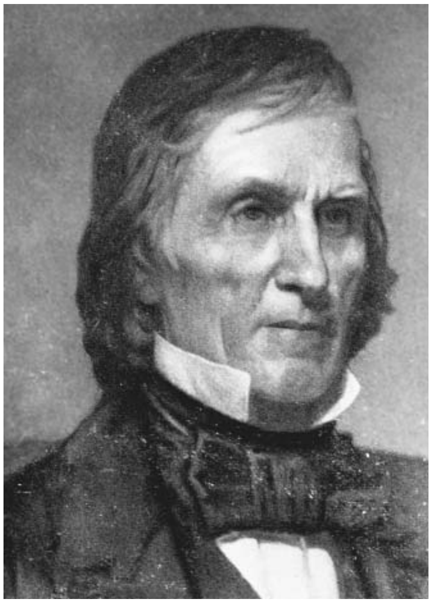
Gibbs, Josiah Willard

AMERICAN MATHEMATICIAN AND PHYSICIST
1839–1903

Josiah Willard Gibbs was born in New Haven, Connecticut, on February 11, 1839, into a family of academics whose connection to higher education dates back to the 1600s. Gibbs entered Yale University (where his father served as librarian) in 1854, graduated in 1858 with distinction in mathematics and Latin, and continued his studies there, in 1863 earning the first Ph.D. in engineering in the United States. He was appointed tutor and taught Latin and natural philosophy until 1866, whereupon he left New Haven to study in Europe. He attended lectures by the eminent scientists of Paris, Berlin, and Heidelberg, returning home in 1869. He was appointed professor of mathematical physics at Yale in 1871, a post he held until his death in 1903.

In 1873 Gibbs published the first two of his revolutionary papers, which unveiled graphical methods for visualizing properties such as stability, equilibrium, and critical states for thermodynamic systems. One of his major accomplishments was showing the usefulness of the "entropy" quantity that the German mathematical physicist Rudolf Clausius had posited in 1865. This was followed in 1876 by his famous "On the Equilibrium of Heterogeneous Substances" paper, in which he introduced the field of chemical thermodynamics, advancing the concept of chemical potential. Gibbs's free energy G determines whether it is favorable that chemicals will react. Gibbs employed a completely general treatment, making almost no assumptions about the properties of the interacting substances. His celebrated phase rule allowed for the identification of the number of coexisting phases in a system.


American physicist Josiah Willard Gibbs, creator of the field of chemical thermodynamics.

When one aspect of Gibbs's work in thermodynamics, the phase rule, is considered, just how important the discovery of this theoretical system was becomes clear. The phase rule allows one to determine the number of coexisting phases of any system, no matter how complicated. The rule relates the number of independently changeable intensive variables, or degrees of freedom, F, the number of components (i.e., substances) C, and the number of phases in equilibrium P, as follows:

$$F = C - P + 2$$

Thus, in a one-component system (such as pure water), at temperature and pressures where one phase is present ($F = 1 - 1 + 2 = 2$), those variables can be varied independently (carving out an area of coexistence on a phase diagram). In order to keep two phases in coexistence ($F = 1 - 2 + 2 = 1$), like water and ice, varying the pressure necessitates a specific change in the temperature (which forms a coexistence line on a phase diagram). Where all three phases (ice, water, and vapor) coexist, there are no degrees of freedom, which translates to a single point, the triple point, on a phase diagram. In other words, there is only one temperature and pressure where all three phases of water are in equilibrium. More complicated systems have more intricate phase diagrams, but the phase rule allows one to, relatively, easily determine the phase properties of any system.

Due in part to his mathematically demanding and abstract style of writing, and also since his papers were published in the obscure *Transactions of the Connecticut Academy of Arts and Sciences*, Gibbs's work was not immediately embraced by the scientific community, with the notable exception of the Scottish physicist James Clerk Maxwell. Consequently, many of Gibbs's results were not discovered until years or decades later by scientists ignorant of his work.

quantum mechanics: theoretical model to describe atoms and molecules by wave functions

Gibbs also wrote an influential book on statistical mechanics, which developed a molecular theory of thermodynamic properties from first principles, with a treatment that was general enough to accommodate **quantum mechanics**, a theory that had not even been imagined yet. He championed the now standard use of vector notation over William Rowan Hamilton's quaternion algebra and wrote several seminal papers on electromagnetism in the 1880s that supported Maxwell's theory. SEE ALSO EQUILIBRIUM; MAXWELL, JAMES CLERK; THERMODYNAMICS.

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Glass

Glass is a state of matter. It is a solid produced by cooling molten material so that the internal arrangement of atoms, or molecules, remains in a random or disordered state, similar to the arrangement in a liquid. Such a solid is said to be *amorphous* or glassy. Ordinary solids, by contrast, have regular crystalline structures. The difference is illustrated in Figure 1.

Many materials can be made to exist as glasses. Hard candies, for example, consist primarily of sugar in the glassy state. What the term "glass" means to most people, however, is a product made from silica (SiO_2). The

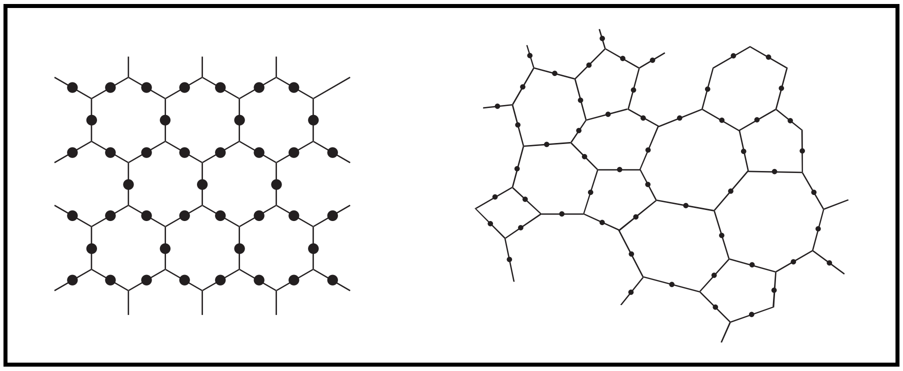

Figure 1. Structures of a typical solid (l.) and glass (r.).

common form of silica is sand, but it also occurs in nature in a crystalline form known as quartz.

Pure silica can produce an excellent glass, but it is very high-melting (1,723°C, or 3,133°F), and the melt is so extremely viscous that it is difficult to handle. All common glasses contain other ingredients that make the silica easier to melt and the hot liquid easier to shape.

Natural Glass

Probably as early as 75,000 B.C.E., long before human beings had learned how to make glass, they had used natural glass to fashion knives, arrowheads, and other useful articles. The most common natural glass is obsidian, formed when the heat of volcanoes melts rocks such as granite, which then become glassy upon cooling. Other natural glasses are pumice, a glassy foam produced from lava; fulgurites, glass tubes formed by lightning striking sand or sandy soil; and tektites, lumps or beads of glass probably formed during meteoric impacts.

Manmade (Synthetic) Glass

When, where, or how human beings discovered how to make glass is not known. Very small dark-colored beads of glass have been dated back to 4000 B.C.E. These may well have been by-products of copper smelting or pottery glazing. By 2500 B.C.E. small pieces of true synthetic glass appeared in areas such as Mesopotamia, but an actual glass industry did not appear until about 1500 B.C.E. in Egypt. By this time various small vases, cosmetic jars, and jewelry items made of glass had begun to appear.

All the ancient glasses were based on silica (sand), modified with considerable amounts of various metal oxides, mainly soda (Na_2O) and lime (CaO). This is still the most common glass being used today. It is known as soda lime glass. However, the ancient glass was usually colored and opaque due to the presence of various impurities, whereas most modern glass has the useful property of transparency.

Hundreds of thousands of different glass compositions have been devised, and they have been used in different ways. Much has been learned about which combination of chemicals will make the best glass for a particular purpose. For example, in 1664 an Englishman named Ravenscroft found that adding lead oxide (PbO) to a glass melt produced a brilliant glass that was much easier to melt and to shape. Since that time lead glass has been used to make fine crystal bowls and goblets and many kinds of art glass.

An important kind of glass was developed in the early 1900s to solve a serious problem—the inability of glass to withstand temperature shock. This failure resulted in tragic accidents in the early days of the railroads. Glass lanterns used as signals would get very hot, and then, if it started to rain, the rapid cooling would sometimes cause the glass to break and the signal to fail. The problem was solved by replacing much of the soda in the glass with boron oxide (B_2O_3). The resulting glass, called borosilicate, contains about 12 percent boron oxide and can withstand a temperature variation of 200°C (392°F). It also has greater chemical durability than soda lime glass. Today borosilicate glass is used in most laboratory glassware (beakers, flasks, test tubes, etc.) and in glass kitchen bakeware.

For even greater heat shock resistance and chemical durability, alumina (Al_2O_3) can be used instead of boron oxide. The resultant aluminosilicate glass has such resistance to heat shock that it can be used directly on the heating element of the kitchen stovetop. It is also used to make the special bottles used for liquid pharmaceutical prescriptions, and to produce the glass thread that is woven into fiberglass fabric.

High silica glass (96.5–100% silica) remains difficult to make because of the very high melting point of pure silica. However, it is made for special purposes because of its outstanding durability, excellent resistance to thermal shock or chemical attack, and ability to transmit ultraviolet light (an ability that ordinary glass does not have). Spacecraft windows, made of 100 percent silica, can withstand temperatures as high as 1,200°C (2,192°F). Table 1 lists the five major types of glass along with properties and uses.

Glass Composition. The making of glass involves three basic types of ingredients: formers, fluxes, and stabilizers. The glass former is the key component in the structure of a glassy material. The former used in most glasses is silica (SiO_2). Pure silica is difficult to melt because of its extremely high melting point (1,723°C, or 3,133°F), but fluxes can be added to lower the melting temperature. Other glass formers with much lower melting points (400°C–600°C, or 752–1,112°F) are boric oxide (B_2O_3) and phosphorus pentoxide (P_2O_5). These are easily melted, but because their glass products dissolve in water, they have limited usefulness.

Most silica glasses contain an added flux, so that the silica can be melted at a much lower temperature (800°C–900°C, or 1,472–1,652°F). Standard fluxes include soda (Na_2O), potash (K_2O), and lithia (Li_2O). Frequently the flux is added as a carbonate substance (e.g., Na_2CO_3), the CO_2 being driven off during heating. Glasses containing only silica and a flux, however, have poor durability and are often water-soluble.

To make glasses stronger and more durable, stabilizers are added. The most common stabilizer is lime (CaO), but others are magnesia (MgO), baria (BaO), and litharge (PbO). The most common glass, made in largest amounts by both ancient and modern glassmakers, is based on silica as the glass former, soda as the flux, and lime as the stabilizer. It is the glass used to make windows, bottles, jars, and lightbulbs.

Colored Glass. The natural glasses used by the ancients were all dark in color, usually ranging from olive green or brown to jet black. The color was

MAJOR GLASS TYPES AND THEIR USES

Glass Type	Properties	Limitations	Uses
Soda lime	Inexpensive; easy to melt and shape; most widely used glass	Poor durability; not chemically resistant; poor thermal shock resistance	Windows; bottles; light bulbs; jars
Lead glass (often 20–30% Pb oxide)	High density; brilliant; very easy to melt, shape, cut, and engrave	Poor durability; easily scratched	Fine crystal radiation windows; TV tube parts
Borosilicate (usually 5–13% B_2O_3)	Very good thermal shock resistance and chemical durability; easy to melt and shape	Not suitable for long-term high temperature use	Labware; kitchenware; special light bulbs; glass pipe; sealed beam headlights
Aluminosilicate (usually 5–10% Al_2O_3)	Excellent thermal resistance; durability	More difficult to melt and shape than borosilicate	Top-of-stove cookware; high quality fiberglass
High silica (Vycor 96.5%; fused quartz 100%)	Outstanding thermal resistance	Difficult to make; very expensive	Spacecraft windows; labware; fiber optics

Table 1. Major glass types and their uses.

due to the presence of significant amounts of metal impurities, especially iron. Even today the ubiquitous presence of iron in nature causes most ordinary glass to have a slight greenish cast.

Many standard glass colorants are oxides of metals such as cobalt (blue), chromium (green), and manganese (violet). Yellow glass is usually made with cadmium sulfide, and red or pink glass usually contains selenium, although some ruby-colored glass has had gold added. The coloring of glass is not a simple subject. Glass color depends not only on which elements are added, but also on the composition of the glass, and on whether the furnace used was in an oxidizing or reducing mode. Copper, for example, can produce blue, green, or opaque red glass, depending on melting conditions.

The Egyptians of 1500 B.C.E. knew that they could make brightly colored glasses by adding certain metals (or their compounds) to the glass melt. The ancient Romans continued the science of making colored glass and expanded it. By the fourth century C.E. the Romans had learned how to produce a dichroic (two-color) glass. The most famous dichroic glass article left by the Romans is the Lycurgus Cup (now at the British Museum). It is green in reflected light (with the lamp in front of the cup), but red in transmitted light (the lamp behind the cup). This unusual glass contains microscopic particles of gold and silver.

Glass Forming

Ancient Methods. Shaping hot, molten glass into useful articles has long been a challenge. Molten glass is extremely hot, caustic, sticky, and difficult to handle. In the period extending from about 2000 B.C.E. to 50 B.C.E., there were three basic methods used to form glass. One of the earliest and most widely used was core forming. This involved distributing molten glass around a clay core on a metal rod. The rod with the clay core could either be dipped into molten glass, or the hot liquid glass could simply be poured over it. The outer glass coating was then rolled (marvered) on a flat stone surface to smooth it. Often the object was decorated by dribbling more glass, sometimes of a different color, onto its surface. The hot glass was then annealed (cooled slowly so as to relieve thermal stress), and the metal rod was removed and the clay core scraped out.

A second method involved sagging and fusing. It called for taking preformed glass rods or canes (which were often of different colors), placing them in or on top of a mold, and then heating the canes until they sagged and fused together and conformed to the shape of the mold. (Sheets of glass could also be sagged over shaped clay molds.)

The third method was casting, which called for pouring hot, molten glass into a mold. A variation on cast glass was faience, made from powdered quartz blended into molten glass. The mixture might be pressed between two molds to make a cast vessel such as a bowl.

All three of these methods were slow, and they generally produced small items that were rather thick. Glass pieces tended to be quite expensive, and, in antiquity, were affordable only by the very wealthy.

Glassblowing. It was probably in the Middle East during the first century B.C.E. that the important technique of glassblowing was discovered. A hollow metal rod (or pipe) was used to pick up a gob of molten glass; the act of blowing into the pipe generated a bubble of glass. If the bubble were blown into a mold, the molten glass could be given a desired shape. Wooden paddles and pincers were used to refine the shape even further. The blowing procedure was used to make glass objects that were larger and thinner than those that had been made previously, and it was much faster than previous glass-forming methods. As glass pieces became easier to make, they became cheaper and more available. The ancient Romans became particularly skillful at glassblowing. More glass was produced and used in the Roman world than in any other civilization of antiquity. During the Middle Ages, there was a great expansion of glassblowing activity, especially in Venice, the Middle East, and European countries such as Spain and Germany.

Some Modern Methods. Since the nineteenth century, many centuries-old glass-forming methods have been mechanized, greatly increasing the rate of production of glass objects, and lowering the prices of these objects. For example, the “ribbon machine,” developed in the 1920s for the automatic glassblowing of lightbulbs, is a milestone of mechanical glass forming. In the ribbon machine, puffs of air blow glass bubbles from a rapidly moving ribbon of molten glass into a moving stream of molds that give the bulbs their shape and then release them. Small lightbulb blanks can be made at the rate of 1,000 per minute.

With so many millions of windows in buildings and vehicles everywhere, we tend to take sheets of flat glass for granted. Throughout most of human history, however, there were no sheets of flat, transparent glass. Even as recently as the eighteenth century, glass windows were quite uncommon.

In a very limited way glass windows did start to appear in the Roman world during the third century, but they were generally small glass fragments set in bronze or wooden frames. In that era most windows were not glass, but were thin sheets of translucent horn or marble, or perhaps panes of mica (isinglass). Around 600 C.E., during the Byzantine period, glass windows (usually made of small pieces of colored glass) began to appear in the large churches, but glass windows in houses and other secular buildings remained quite rare until the end of the eighteenth century.

The principal method for making flat glass during the 1700s called for blowing a hot glass bubble, securing an iron rod to the bubble's other side, and then cutting the bubble free from the blowing pipe. The tulip-shaped hot glass was then rotated rapidly around the iron rod axis until the centrifugal force forced the glass tulip to open up and form a disk. The rod was then removed from the glass (leaving a spot in the middle of the glass disk that looked rather like a bull's eye). This method was the source of the old "bull's-eye" windows that can still sometimes be found in English pubs. The windows were limited in size and poor in optical quality (besides having a bull's-eye at their centers).

The chief method for making flat glass during the 1800s was the cylinder method. The first step was to blow a large glass bubble (compressed air was often used); it would then be swung back and forth until the bubble became elongated and acquired a cylindrical shape; finally the cylinder was split lengthwise, reheated, and allowed to flatten on an iron table. The resulting pane of glass was not really flat, and it had a lot of optical distortion, but the method was used widely to make sheet glass. For example, it was used to produce the 300,000 panes of glass that were used to build London's Crystal Palace, the huge greenhouse constructed for the London World's Fair Exhibition of 1851.

By the twentieth century these methods were replaced by an innovative technique invented by a Belgian named Foucault, who had learned how to draw up continuous sheets from a tank filled with molten glass. Even this glass was of nonuniform thickness and had some roughness at its surface, therefore, for high quality flat glass, it had to be ground and polished.

Then, in 1959, the Pilkington Glass Works in Britain introduced the "float glass" process. In the float process, molten glass is allowed to flow continuously onto a mirrorlike surface of molten tin at 1,000ºC (1,832ºF). At this temperature the glass spreads out and becomes a layer that is about 6 millimeter (1/4 inch) thick. If the layer is stretched as it cools, a thickness of 2 millimeter (0.08 inch) can be achieved. The glass is allowed to advance on the hot liquid tin until, at 600ºC (1,112ºF), it becomes solid enough to be lifted off the molten tin surface. It is then annealed (heated to relieve any strain) before being cut into desired sheet lengths. The float glass method rapidly replaced the Foucault drawing process, and today it is the standard method for making flat glass. A large modern float glass plant can produce 5,000 tons of glass sheet per week, and it can be operated 24 hours a day, 365 days a year, for several years before serious repairs are apt to be needed. Float glass has uniform thickness and bright fire-polished surfaces that need no grinding or polishing.

The drawing of glass fibers had long been of interest, but glass fibers found little use until the twentieth century. Articles such as wedding gowns made from glass fiber cloth were largely curiosities, made for show rather than use. In the 1930s glass researchers learned to feed molten glass into platinum bushings having hundreds of tiny holes. Fine glass filaments of 10 to 50 microns were rapidly drawn downward and assembled as bundles or strands of glass fiber. Today a major use of glass cloth or filaments is to strengthen the plastics used to make fiberglass-reinforced composites. These composites are widely used in making boats, from canoes to yachts, and bodies for cars, such as the Corvette.

An even larger poundage market is that of glass wool insulation. In a process much like that used to make cotton candy, fine glass fibers are spun, sprayed with an organic bonding agent, and then heat-cured and cut into mats of various sizes, to be used for insulating buildings and appliances.

Surely the most significant glass fiber development in recent times is fiber optics, or optical wave guides. These ultrapure, very fine glass fibers are a most crucial part of modern communications technology, wherein glass fibers link telephones, televisions, and computers. A single strand of glass optical fiber that has a protective plastic coating looks much like a human hair. The glass fiber has an inner core of ultrapure fused silica, which is coated with another silica glass that acts as a light-refractive barrier. Lasers are used to convert sound waves and electrical impulses to pulses of light that are sent, static-free, through the inner glass core. Glass fibers can transmit many times more information than can be carried by charges moving in a copper wire. In fact, one pound of glass optical wave guides can transmit as much information as can be transmitted via 200 tons of copper wire. Today millions of miles of optic fibers are crisscrossing not only the United States, but also the entire planet.

Windows need to be cleaned. In 2000 a new glass that largely cleans itself when it comes into contact with rain was introduced. This low-maintenance glass was developed by Pilkington Glass Works, the company that invented the float process. It is made by depositing a microscopically thin coating of titanium dioxide (TiO_2) on hot sheet glass during its manufacture in the float process. As dirt collects on the window, the Sun's ultraviolet rays promote a catalytic reaction at the glass surface that breaks down and loosens surface dirt. SEE ALSO Ceramics; Gemstones; Minerals.

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Global Warming

The term "global warming" refers to an increase in Earth's mean global temperature because a part of Earth's outgoing infrared radiation is retained by several trace gases in the atmosphere whose concentrations have been increasing because of human industrial, commercial, and agricultural activities. These gases have the ability to absorb radiation, leading to the tendency of the atmosphere to create warmer climates than would otherwise be the case. The most important naturally occurring trace gases that have the ability to absorb infrared radiation are water vapor (H_2O), carbon dioxide (CO_2), methane (CH_4), nitrous oxide (N_2O), and ozone (O_3). In addition, there are some industrial gases that are extremely effective absorbers of the radiation. Important among these are **chlorofluorocarbons (CFCs)**, perfluorocarbons, hydrochlorofluorocarbons, hydrofluorocarbons (HFCs), and sulfur hexafluoride (SF_6). These gases are analogous to the glass in a greenhouse, which also leads to the net trapping of infrared radiation, hence the terms "greenhouse gases" (GHGs) and "**greenhouse effect**." These GHGs act as a partial blanket for the thermal radiation from the surface and make the atmosphere warmer than it would otherwise be. Before human intervention, Earth's radiation balance was in **equilibrium**, resulting in a mean average temperature of Earth at 15°C (59°F). Without the presence of naturally occurring GHGs, Earth's average surface temperature would have been −18°C (−0.4°F). This difference of 33°C (91.4°F) is due to the natural greenhouse effect, which has made Earth a habitable planet. Although the level of naturally occurring GHGs may change naturally over time, their concentration has steadily increased since the **Industrial Revolution** that began around 1750, because of fossil fuel **combustion**, deforestation, **biomass** burning, drainage of wetlands, conversion of natural into agricultural ecosystems, and plowing/cultivation of soil.

chlorofluorocarbon (CFC): compound that contains carbon, chlorine, and fluorine atoms, which remove ozone in the upper atmosphere

greenhouse effect: presence of carbon dioxide in the atmosphere prevents heat from escaping, thereby raising Earth's temperature

equilibrium: condition in which two opposite reactions are occurring at the same speed, so that concentrations of the products and reactants do not change

Industrial Revolution: widespread replacement of hand tools by power-driven machines, beginning about 1750 (especially in England)

combustion: burning, the reaction with oxygen

biomass: collection of living matter

The concentration of CO_2 has increased from about 280 parts per million by volume (ppmv) in the preindustrial era to about 370 ppm in 2000, and is increasing at the rate of about 1.5 ppm/yr (0.4 percent/yr). The atmospheric concentration of CH_4 has increased from 700 parts per billion by volume (ppbv) to 1,720 ppbv, and is increasing at the rate of 10 ppbv/yr (0.6 percent/yr). Similarly, the concentration of N_2O has increased from 275 ppbv to 312 ppbv and is increasing at the rate of about 0.8 ppbv/yr (0.25 percent/yr) (Bruce, Lee, and Haites 1996). Because of the successful implementation of the Montreal Protocol in 1987, the concentration of industrial gases has been decreasing.

There are three anthropogenic human-derived sources of atmospheric enrichment of CO_2: (1) fossil fuel combustion; (2) cement manufacturing; and (3) land use change involving deforestation, biomass burning, and cultivation. Fossil fuel combustion annually emits 6.22 Pg C (1 Pg = 1 billion metric tons) as CO_2, 46 to 155 Tg of C (1 Tg = 1 million metric tons) as CH_4, and 0.7 to 1.8 Tg N as N_2O and NO_x. The fossil fuel emission has steadily increased over the last 150 years. The CO_2-C emission from fossil fuel combustion was negligible in 1850, 1,850 Tg/yr in 1900, 1.7 Pg/yr in 1950, and 6.2 Pg/yr in 1995 (Hansen, et al. 1998, pp. 12753–12758). Cement manufacturing emits 0.2 Pg C/yr as CO_2. Tropical deforestation and soil cultivation annually emit 0.6 to 2.6 Pg C as CO_2, 160 to 460 Tg of C as CH_4, and 2.2 to 6.8 Tg N as NO_x (Harvey 2000, pp. 16–20). From 1850 to 1998, approximately 270 (±30) Pg C has been emitted as CO_2 by fossil fuel combustion and cement production. During the same time, about 136 (±55) Pg has been emitted as a result of deforestation and land use change, of which 78 (±17 Pg) is due to depletion of the soil organic carbon pool (Watson, et al. 2000, p. 4; Lal 1999, p. 317).

The alteration in Earth's radiation budget because of an increase in atmospheric concentration of GHGs is referred to as "radiative forcing," and is measured in w/m^2. The radiative forcing of three gases (CO_2, CH_4, and N_2O) since the preindustrial era is 2.45 w/m^2, due to the accelerated greenhouse effect or global warming. The GHGs differ with regard to their radiative forcing and their life span, or residence time in the atmosphere. This relative ability of GHGs is called the global warming potential or GWP. The GWP is computed relative to CO_2, and is 1 for CO_2, 21 for CH_4, 210 for N_2O, 1,800 for O_3, and 4,000 to 12,000 for CFCs. It is estimated that the mean global temperature has increased by about 0.5°C (32.9°F) since the preindustrial era. With business as usual, the radiation budget of Earth may change within a short span of several decades to a century, with an attendant increase in Earth's mean temperature of 1 to 4°C (33.8 to 39.2°F). The projected increase will be less in the tropics than in the boreal, temperate, and cold regions. The greenhouse effect is tolerable (i.e., the biomes or ecological communities comprising plants and animals can adapt) if the rate of increase in Earth's mean temperature is about 0.1°C (32.18°F) per decade.

World soils constitute the third largest global C pool (after oceanic and geologic), and comprise 1,550 Pg of soil organic carbon (SOC) and 750 Pg of soil inorganic carbon (SIC). Thus, the soil C pool is 3.2 times the atmospheric pool (720 Pg), and 4.1 times the biotic pool (560 Pg). The C depleted from the SOC pool can be resequestered through adoption of appropriate land use and soil/crop/vegetation management practices (Lal and Bruce 1999, p. 182; Lal 2001a, pp. 171–172). Restoration of degraded soils and ecosystems and desertification control have a potential to sequester

C in soil and the biota and to decrease the rate of enrichment of GHGs in the atmosphere (Lal 2001b, p. 52; 2001c, p. 23).

There are short-term and long-term strategies of mitigating the accelerated greenhouse effect. In the short term, it is important to improve energy use efficiency and to identify strategies of CO_2 sequestration. In the long term, it is important to develop noncarbon fuel sources. Carbon sequestration in soil and vegetation through restoration of degraded soils and the ecosystem and adoption of appropriate land uses is a winning strategy. SEE ALSO Air Pollution.

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Globular Protein

In a globular protein, the amino acid chain twists and folds in a manner that enhances the protein's solubility in water by placing polar groups of atoms at the protein's surface (where they can participate in attractive interactions with water molecules). This twisting and folding that determine the overall shape of a protein molecule (its tertiary structure) are due largely to the very complex interplay of **intramolecular forces** that exists among different groups of atoms within the molecule, and to intermolecular forces acting between groups of atoms on the protein and molecules in the protein's immediate surroundings. Some of the common amino acids have polar side chains; this polarity is the result of chemical bonds between atoms in these side chains that have very different electronegativities (for instance, oxygen and hydrogen). A protein's polar side chains tend to exert strong attractive forces toward other polar groups of atoms within the protein molecule, or toward polar molecules in the protein's surroundings. Similarly, **nonpolar** side chains exert attractive forces (of a different nature) toward other nonpolar side chains within the protein. The shape assumed by a globular protein molecule tends to maximize both types of attractive forces, whereby

intramolecular force: force that arises within molecules—essentially the force associated with chemical bonds

nonpolar: molecule, or portion of a molecule, that does not have a permanent, electric dipole

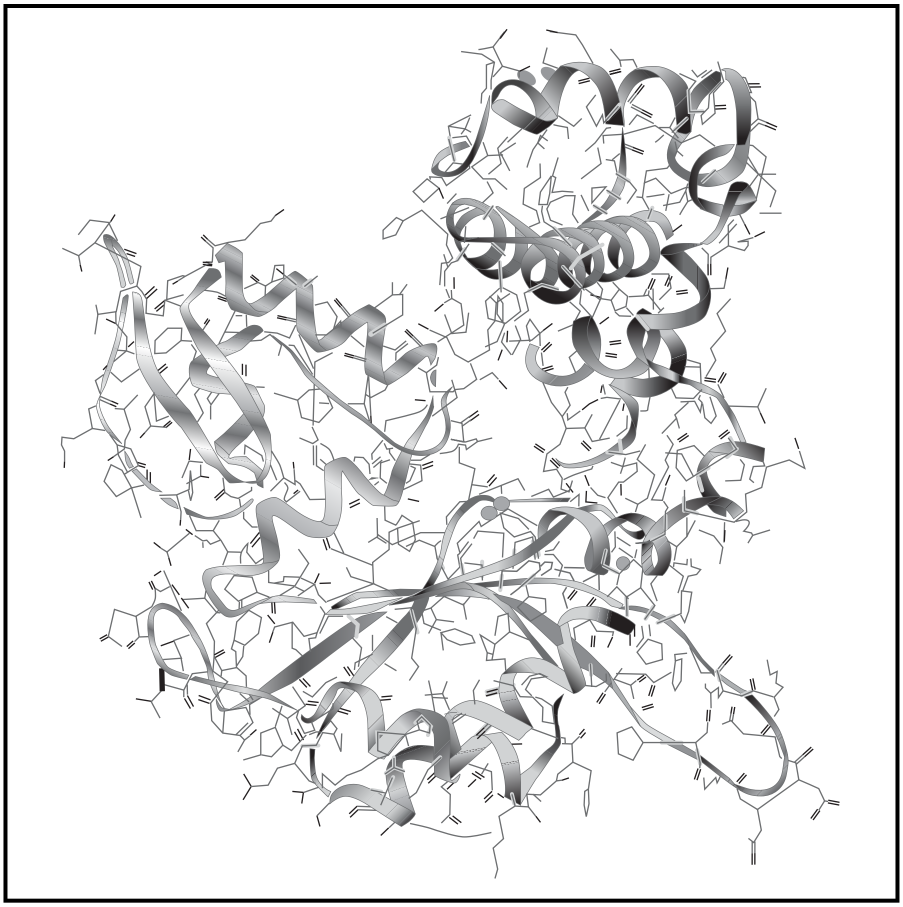

Figure 1. The 3-dimensional molecular structure of the globular protein polymerase β. The ribbon represents the backbone of the amino acid chain with the various amino acids depicted by shading. The side chains of the amino acids fill in the structure.

nonpolar side chains "point" inward and interact with one another and polar side chains are oriented outward such that they are exposed to adjacent polar water molecules. Over the last few decades, molecular shape and structure have been experimentally determined for several thousand proteins.

The aqueous solubility of globular proteins allows them to exist in biological fluids as individual molecules or in small clusters and to accomplish a wide range of critical biological functions, for example, the enzymatic **catalysis** of chemical reactions. Globular proteins also function as **antibodies** in the body's immune system and as transport vehicles for other molecules in circulating blood, and they are heavily involved in the replication and repair of **DNA**. Figure 1 shows the molecular structure of polymerase β, a much-studied globular protein that catalyzes reactions having to do with the repair of damaged DNA. The structure of polymerase β was determined by Huguette Pelletier and her coworkers using the technique of x-ray diffraction at the University of California, San Diego. SEE ALSO AMINO ACID; PROTEINS; TERTIARY STRUCTURE.

catalysis: the action or effect of a substance in increasing the rate of a reaction without itself being converted

antibody: protein molecule that recognizes external agents in the body and binds to them as part of the immune response of the body

DNA: deoxyribonucleic acid—the natural polymer that stores genetic information in the nucleus of a cell

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Glycolysis

Glycolysis is the sequence of enzymatic reactions that oxidize the six-carbon sugar **glucose** into two three-carbon compounds with the production of a small amount of **adenosine triphosphate (ATP)**. Glycolysis has two basic functions in the cell. First, it metabolizes simple six-carbon sugars to smaller three-carbon compounds that are then either fully metabolized by the mitochondria to produce carbon dioxide and a large amount of ATP or used for the **synthesis** of fat for storage. Second, glycolysis functions to produce

glucose: common hexose monosaccharide; monomer of starch and cellulose; also called grape sugar, blood sugar, or dextrose

adenosine triphosphate (ATP): molecule formed by the condensation of adenine, ribose, and triphosphoric acid, HOP(O)OH–O–(O)OH–OP(O)OH–OH; it is a key compound in the mediation of energy in both plants and animals

synthesis: combination of starting materials to form a desired product

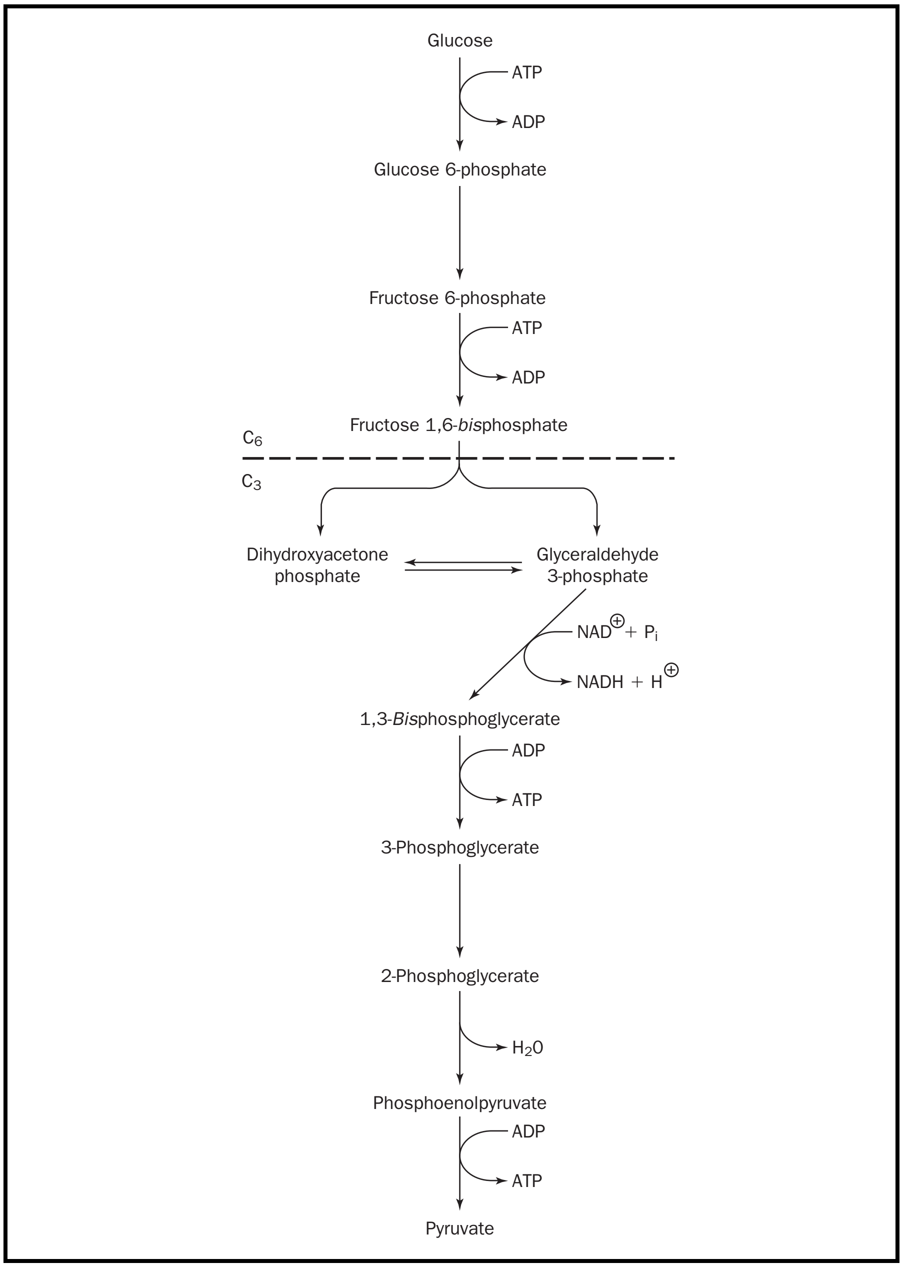

Figure 1. The glycolytic pathway.

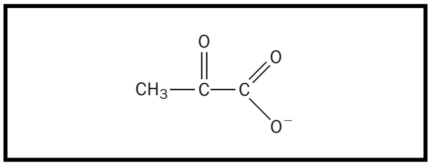

Figure 2. Structure of pyruvate.

monosaccharide: one class of the natural products called carbohydrates with the general formula $C_x(H_2O)_y$; monosaccharides have a weak sweet taste, are readily soluble in water, and are called sugars

galactose: six-carbon sugar

metabolism: the complete range of biochemical processes that take place within living organisms; comprises processes that produce complex substances from simpler components, with a consequent use of energy (anabolism), and those which break down complex food molecules, thus liberating energy (catabolism)

oxidation: process that involves the loss of electrons (or the addition of an oxygen atom)

adenine: one of the purine bases found in nucleic acids, $C_5H_5N_5$

pyruvate: anion of pyruvic acid produced by the reaction of oxygen with lactic acid after strenuous exercise

metabolize: performing metabolism—the processes that produce complex substances from simpler components, with a consequent use of energy (anabolism) and those which break down complex food molecules, thus liberating energy (catabolism)

hydrophilic: a part of a molecule having an affinity for water

a small amount of ATP, which is essential for some cells solely dependent on that pathway for the generation of energy.

The glycolytic pathway is nearly ubiquitous, being found in every cell of virtually all living creatures. It is catalyzed by soluble enzymes located in the cytosol of cells. Although the glycolytic pathway is most commonly thought of as metabolizing glucose, other common **monosaccharides** such as fructose, **galactose**, and mannose are also metabolized by it. The glycolytic pathway operates in both the presence (aerobic) or absence of oxygen (anaerobic).

The **metabolism** of fuel molecules in the cell can be thought of as an **oxidation** process. In glycolysis, glucose is the fuel molecule being oxidized. As the glucose is oxidized by the glycolytic enzymes, the coenzyme nicotinamide **adenine** dinucleotide (NAD^+) is converted from its oxidized to reduced form (NAD^+ to NADH). When oxygen is available (aerobic conditions), mitochondria in the cell can reoxidize to NADH to NAD^+. However, if either oxygen levels are insufficient (anaerobic conditions) or mitochondrial activity is absent, NADH must be reoxidized by the cell using some other mechanism. In animal cells, the reoxidation of NADH is accomplished by reducing **pyruvate**, the end-product of glycolysis, to form lactic acid. This process is known as anaerobic glycolysis. During vigorous exercise, skeletal muscle relies heavily on it. In yeast, anaerobic conditions result in the production of carbon dioxide and ethanol from pyruvate rather than lactic acid. This process, known as alcoholic fermentation, is the basis of wine production and the reason why bread dough rises.

Although some cells are highly dependent on glycolysis for the generation of ATP, the amount of ATP generated per glucose molecule is actually quite small. Under anaerobic conditions, the metabolism of each glucose molecule yields only two ATPs. In contrast, the complete aerobic metabolism of glucose to carbon dioxide by glycolysis and the Krebs cycle yields up to thirty-eight ATPs. Therefore, in the majority of cells the most important function of glycolysis is to **metabolize** glucose to generate three-carbon compounds that can be utilized by other pathways. The final product of aerobic glycolysis is pyruvate. Pyruvate can be metabolized by pyruvate dehydrogenase to form acetyl coenzyme A (acetyl CoA). Under conditions where energy is needed, acetyl CoA is metabolized by the Krebs cycle to generate carbon dioxide and a large amount of ATP. When the cell does not need energy, acetyl CoA can be used to synthesize fats or amino acids. SEE ALSO INSULIN; KREBS CYCLE.

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Glycoprotein

Glycoproteins are proteins that contain covalently attached sugar residues. The **hydrophilic** and polar characteristics of sugars may dramatically change the chemical characteristics of the protein to which they are attached.

The addition of sugars is often required for a glycoprotein to function properly and reach its ultimate destination in the cell or organism. Glycoproteins are frequently present at the surface of cells where they function as membrane proteins or as part of the extracellular matrix. These cell surface glycoproteins play a critical role in cell–cell interactions and the mechanisms of infection by bacteria and viruses.

There are three types of glycoproteins based on their structure and the mechanism of synthesis: N-linked glycoproteins, O-linked glycoproteins, and nonenzymatic glycosylated glycoproteins.

N-linked glycoproteins are synthesized and modified within two membrane-bound organelles in the cell, the rough **endoplasmic reticulum** and the Golgi apparatus. The protein component of the glycoprotein is assembled on the surface of the rough endoplasmic reticulum by the sequential addition of amino acids, creating a linear polymer of amino acids called a **polypeptide**. Twenty different amino acids can be used for the synthesis of polypeptides. The specific order of the amino acids in the polypeptide is critical to its function and is referred to as the amino acid sequence. One of the twenty amino acids used for the synthesis of polypeptides, asparagine ($C_4H_8N_2O_3$), is essential for the synthesis of N-linked glycoproteins.

endoplasmic reticulum: internal membrane system that forms a net-like array of channels and interconnections of organelles within the cytoplasm of eukaryotic cells

polypeptide: compound containing two or more amide units—C(O)NH—produced by the condensation of two or more amino acids

N-linked glycoproteins have carbohydrates attached to the R side chain of asparagine residues within a polypeptide. The carbohydrate is always located in amino acid sequences, where the asparagine is followed by some other amino acid and then a serine or threonine residue (-Asn-Xaa-Ser/Thr). Carbohydrate is not attached to the polypeptide one sugar at a time. Rather, a large preformed carbohydrate containing fourteen or more sugar residues is attached to the asparagine as the protein is being translated in the rough endoplasmic reticulum. The carbohydrate on the glycoprotein is then modified by enzymes that remove some sugars and attach others as the newly formed glycoprotein moves from the rough endoplasmic reticulum to the Golgi apparatus and other locations in the cell. Many N-linked glycoproteins eventually become part of the cell membrane or are secreted by the cell.

O-linked glycoproteins are usually synthesized by the addition of sugar residues to the hydroxyl side chain of serine or threonine residues in polypeptides in the Golgi apparatus. Unlike N-linked glycoproteins, O-linked glycoproteins are synthesized by the addition of a single sugar residue at a time. Many O-linked glycoproteins are secreted by the cell to become a part of the extracellular matrix that surrounds it.

Nonenzymatic glycosylation or glycation creates glycoproteins by the chemical addition of sugars to polypeptides. Since this type of glycosylation is nonenzymatic, the factors that control glycosylation are simply time and the concentration of sugar. Older proteins are more glycosylated, and people with higher circulating levels of glucose experience higher levels of nonenzymatic glycosylation. This is the basis of the glycosylated hemoglobin A1c diagnostic test used for the monitoring and long-term maintenance of blood sugar levels in diabetics. SEE ALSO CONCENTRATION GRADIENT; PROTEINS.

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79
Au
GOLD
196.96654

Gold

MELTING POINT: **1,064.18°C**
BOILING POINT: **2,808°C**
DENSITY: **19.32 g/cm^3**
MOST COMMON IONS: **Au$^+$, Au^{3+},**

Gold is a soft, malleable yellow **metal**. If finely divided, it may be black, ruby, or purple. The name of the element is derived from the Anglo-Saxon word *geolo*, meaning "yellow." The symbol Au is derived from the Latin word *aurum*, meaning "shining dawn."

metal: element or other substance the solid phase of which is characterized by high thermal and electrical conductivities

ductile: property of a substance that permits it to be drawn into wires

reagent: chemical used to cause a specific chemical reaction

Gold is the most malleable and **ductile** metal known. Approximately 28 grams (1 ounce) of gold can be hammered to form a piece that is 28 square meters (300 square feet). It is a good conductor of heat and electricity, and unreactive in air and most **reagents**. It forms ionic compounds primarily as a +3 ion; the most common compounds are gold (III) chloride ($AuCl_3$), and chlorauric acid ($HAuCl_4$).

The relative abundance of gold is 0.004 part per million (ppm) in Earth's crust. Deposits of the metal are found in South Africa, Siberia, North America, and South America. Gold has one naturally occurring **isotope** (^{197}Au) and forty-five synthetic isotopes.

isotope: form of an atom that differs by the number of neutrons in the nucleus

Found in association with quartz or pyrite, gold occurs in veins and is traditionally isolated from rocks by panning or sluicing; these techniques take advantage of gold's high density. A modern method of isolation is the cyanide process, in which gold is leached from crushed rock with an aerated solution of sodium cyanide. The gold then precipitates upon addition of zinc dust and is purified by electrolytic refining.

Gold was used as early as the late Stone Age for ornamental purposes (e.g., jewelry and plating) and more recently as a monetary standard. It is a component of electrical connectors in computer equipment due to its high electrical conductivity. Its unreactivity in air leads to its use for corrosion-free contacts in electrical connections. As an excellent conductor of heat, it is used in the main engine nozzle of the space shuttle. Since gold is the most reflective of all metals, it is used as a coating for space satellites, face shields for astronauts, and windows. Chlorauric acid is used in photography; disodium aurothiomalate is given as a treatment for arthritis. SEE ALSO INORGANIC CHEMISTRY; RUTHERFORD, ERNEST.

Catherine H. Banks

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Goodyear, Charles

AMERICAN INVENTOR
1800–1860

American inventor Charles Goodyear, developer of the vulcanization process.

Charles Goodyear was born in New Haven, Connecticut, on December 29, 1800. Goodyear began his work on rubber in 1834, when rubber from Brazilian trees (*Hevea brasiliensis*) was first being imported to the United States in large quantities. He approached a rubber goods manufacturer with an idea for a valve for an inflatable life buoy, but was advised that the company's own products were failing because of the material's inherent flaws. Although it had outstanding qualities, it turned brittle and hard at low temperatures, and worse, into a gooey mass during warm weather.

Goodyear was determined to solve the problems inherent in natural rubber. With no formal training in chemistry, his work was based on trial and error, experimenting with different methods of processing and additives such as magnesia. The solution he discovered resulted partly from serendipity and partly from constant work.

The breakthrough came in 1839 while Goodyear was exhibiting his most recent samples at a general store in Woburn, Massachusetts. When he accidentally dropped a piece on a hot stove, it burned, but the uncharred part was transformed into a smooth, firm material that was not affected by high or low temperature. The additive in the sample was sulfur, but it took Goodyear several months to determine the right combination of heat, pressure, and sulfur to produce a stable compound. He found that the best material was produced when the compound was steam-heated under pressure at 120°C (248°F) for four to six hours. Its first commercial use was as elastic thread in men's shirts.

Goodyear vigorously promoted his product, but was forced to spend large sums of money defending his patent. In Britain, Thomas Hancock had received a patent for **vulcanized rubber** (after Vulcan, the Roman god of fire) a few months before Goodyear applied for his. Although Hancock offered to share his royalties, Goodyear took his claim of sole ownership to court and lost. He also lost his French patent, although he was eventually awarded the Cross of the Legion of Honor by Napoléon III for his important work.

vulcanized rubber: chemical process of mixing rubber with other substances like sulfur; it strengthened rubber so it could be used under hot or cold conditions; discovered by Charles Goodyear

Goodyear invented a material that would eventually be used in thousands of ways and opened the door for a huge industry. Today there is one rubber tree for every two people on Earth. Despite this, he died destitute in New York on July 1, 1860. Although the Goodyear Tire and Rubber Company was named in his honor, Goodyear's descendants had little to do with the rubber industry after his death. SEE ALSO POLYMERS, NATURAL; RUBBER.

Andrew Ede

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Green Chemistry

Green chemistry is also known as environmentally benign chemistry, or sustainable chemistry. Perhaps the most widely accepted definition of green chemistry is the one offered by chemists Paul Anastas and John Warner, who defined green chemistry as the design of chemical products and processes that reduce or eliminate the use and generation of hazardous substances.

Milestones

The Pollution Prevention Act of 1990 set the stage for green chemistry: Its focus is the prevention of pollution at the source rather than the treatment of pollutants after they are formed. This goal became a formal objective of the Environmental Protection Agency (EPA) in 1991. Anastas coined the term "green chemistry" the same year. Two of the most prominent and early advocates of green chemistry were Kenneth Hancock of the National Science Foundation (NSF) and Joe Breen, who after twenty years of service at the EPA then became the first director of the Green Chemistry Institute (GCI) during the late 1990s.

Anastas and Warner formulated the twelve principles of green chemistry in 1998. These serve as guidelines for chemists seeking to lower the ecological footprint of the chemicals they produce and the processes by which such chemicals are made.

Starting in 1996, outstanding examples of green chemistry have been recognized in the United States each year by the Presidential Green Chemistry Challenge (PGCC) awards. These are the only awards in chemistry that are bestowed at the presidential level.

The EPA and the American Chemical Society (ACS) have played a major role in promoting research and development, as well as education, in green chemistry. In 2000 the GCI became a partner of the ACS. Chemical societies around the globe have recognized the importance of green chemistry and promote it through journals, conferences, educational activities, and the formation of GCI chapters. There are GCI chapter affiliates all over the world.

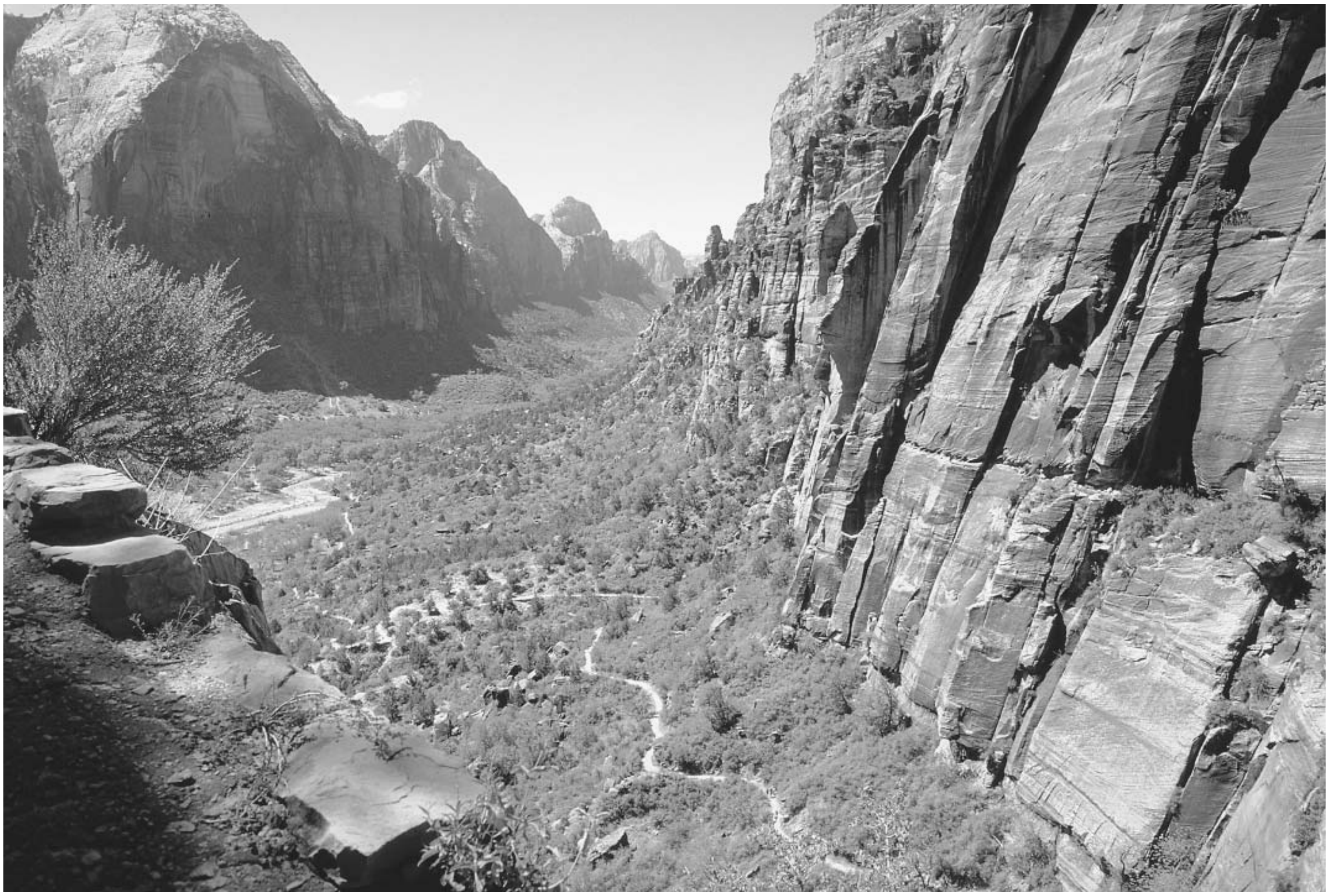
Importance to Industry: The Triple Bottom Line

During the 1990s many industries began to earnestly adopt green chemistry and other sustainable practices. Forward-looking companies realized that the practice of green chemistry not only leads to environmental benefits, but also economic and social benefits. The combination of these three benefits is known as the "triple bottom line" and provides strong encouragement for businesses to develop sustainable products and processes.

The following real-world examples of green chemistry represent the accomplishments of several winners of the PGCC awards. They illustrate how green chemistry impacts a wide array of fields including pharmaceuticals, pesticides, polymers, and many others.

The Concept of Atom Economy

When chemists are considering a compound, they are concerned with the chemical, biological, and physical properties of this compound, and the



Concerns over the pollution of natural resources such as this valley in Zion National Park, Utah prompted the development of green chemistry in the 1990s.

method by which the compound is prepared or its **synthesis**. In order to focus greater attention on waste by-products that are formed during a synthesis, Barry Trost of Stanford University developed the concept of atom economy. This concept deals with the question: How many of the atoms of the reactants are incorporated into the final desired product and how many are wasted by incorporation into by-products? An example of the application of this concept is discussed in the following synthesis of ibuprofen.

synthesis: combination of starting materials to form a desired product

Pharmaceuticals. Ibuprofen is the active ingredient in many **analgesic** and inflammatory drugs such as Advil, Motrin, and Medipren. Beginning in the 1960s, ibuprofen was produced by a six-step synthesis with an atom economy of only 40 percent. This meant that less than half (40 percent) of the weight of all the atoms of the reactants were incorporated in the ibuprofen, and 60 percent were wasted in the formation of unwanted by-products. The annual production of approximately 30 million pounds of ibuprofen by this method resulted in over 40 million pounds of waste. But during the 1990s, the BHC Company developed a new synthesis of ibuprofen with an atom economy of 77 to 99 percent. This synthesis not only produces much less waste, it is also only a three-step process. A pharmaceutical company can thus produce more ibuprofen in less time and with less energy, which results in increased profits.

analgesic: compound that relieves pain, e.g., aspirin

Pesticides. Dichlorodiphenyl trichloroethane (DDT) is one of the most well-known insecticides. During World War II it saved thousands of Allied

THE TWELVE PRINCIPLES OF GREEN CHEMISTRY

1. It is better to prevent waste than to treat or clean up waste after it is formed.

2. Synthetic methods should be designed to maximize the incorporation of all materials used in the process in the final product.

3. Wherever practical, synthetic methodologies should be designed to use and generate substances that possess little or no toxicity to human health and the environment.

4. Chemical products should be designed to preserve efficacy of function while reducing toxicity.

5. The use of auxiliary substances (e.g., solvents, separation agents, etc.) should be made unnecessary whenever possible and innocuous when used.

6. Energy requirements should be recognized for their environmental and economic impacts and should be minimized. Synthetic methods should be conducted at ambient temperature and pressure.

7. A raw material feedstock should be renewable rather than depleting whenever technically and ecomonically practical.

8. Unnecessary derivatization (blocking group, protection/deprotection, temporary modification of physical/chemical processes) should be avoided whenever possible.

9. Catalytic reagents (as selective as possible) are superior to stoichiometric reagents.

10. Chemical products should be designed so that at the end of their function they do not persist in the environment and break down into innocuous degradation products.

11. Analytical methodologies need to be further developed to allow for real-time in-process monitoring and control prior to the formation of hazardous substances.

12. Substances and the form of a substance used in a chemical process should be chosen so as to minimize the potential for chemical accidents, including releases, explosions, and fires.

Source: Anastas, Paul T., and Warner, John C. (1998). *Green Chemistry Theory and Practice.* New York: Oxford University Press.

lives by killing disease-carrying insects, but during the 1960s the significant environmental damage caused by DDT was brought to the public's attention by Rachel Carson in *Silent Spring* (1962). As a result of the controversy generated by this book and other media coverage, the substance's use was banned in the United States in 1973.

During the 1960s and 1970s organophosphates largely replaced organochlorine pesticides such as DDT. These pesticides rapidly **degrade** in the environment, but they are much more toxic to mammals. They are deadly to a wide array of insects and kill not only the target organism but also beneficial insects, such as bees and predatory beetles, and can also be harmful to humans.

degrade: to decompose or reduce to complexity of a chemical

One approach to producing less environmentally harmful pesticides is to use compounds that destroy only the target organisms. One manufacturer, Rohm & Haas, has developed insecticides that mimic a hormone used only by molting insects. Insects that do not molt are not affected, leaving many beneficial insects unharmed.

A more recent strategy for protecting plants from pests and disease involves the use of genetically altered plants. This method is controversial. Concerns include cross-pollination with unaltered plants and the entry of altered plants into the food supply.

Another approach to protecting plants from pests and diseases is to activate their natural defense mechanism against pests or diseases. EDEN Bioscience Corporation has developed what is known as harpin technology. Harpin is a naturally occurring protein that is isolated from genetically altered bacteria. When applied to the leaves and stems of plants, this protein elicits their natural defense systems. The EPA has classified harpin as Category IV, which is reserved for materials with the lowest hazard potential. As an added benefit, harpin also stimulates plant growth.

Polymers. Synthetic polymers or plastics are everywhere. They are used in cars, computers, planes, houses, eyeglasses, paints, bags, appliances, medical devices, carpets, tools, clothing, boats, batteries, and pipes. More than 60 million pounds of polymers are produced in the United States each year. The feedstocks that are used to produce these polymers are virtually all made from petroleum, a nonrenewable resource. Approximately 2.7 percent of all crude oil is used to generate chemical feedstocks.

In order to decrease human consumption of petroleum, chemists have investigated methods for producing polymers from renewable resources such as **biomass**. NatureWorks polylactic acid (PLA) is a polymer of naturally occurring lactic acid (LA), and LA can be produced from the fermentation of corn. The goal is to eventually manufacture this polymer from waste biomass. Another advantage of PLA is that, unlike most synthetic polymers which litter the landscape and pack landfills, it is biodegradable. PLA can also be easily recycled by conversion back into LA. It can replace many petroleum-based polymers in products such as carpets, bags, cups, and textile fibers.

biomass: collection of living matter

Computer Chips. The manufacture of computer chips requires excessive amounts of chemicals, water, and energy. Estimates indicate that the weight of chemicals and fossil fuels required to make a computer chip is 630 times the weight of the chip, as compared to the 2:1 ratio for the manufacture of an automobile. Scientists at the Los Alamos National Laboratory have developed a process that uses supercritical carbon dioxide in one of the steps in chip preparation, and it significantly reduces the quantities of chemicals, energy, and water needed to produce chips.

Dry Cleaning. Condensed **phase** carbon dioxide is also used as a solvent for the dry cleaning of clothes. Although carbon dioxide alone is not a good solvent for oils, waxes, and greases, the use of carbon dioxide in combination with a **surfactant** allows for the replacement of perchloroethylene (which is the solvent used most often to dry clean clothes, although it poses hazards to the environment and is a suspected human carcinogen).

phase: homogeneous state of matter

surfactants: surface-active agents that lower the surface tension of water; e.g., detergents, wetting agents

Other Examples. Some other examples of green chemistry include the following:

- taking chromium and arsenic, which are toxic, out of pressure-treated wood
- using new less toxic chemicals for bleaching paper
- substituting yttrium for lead in auto paint
- using enzymes instead of a strong base for the treatment of cotton fibers

Green chemistry reduces toxicity, minimizes waste, saves energy, and cuts down on the depletion of natural resources. It allows for advances in chemistry to occur in a much more environmentally benign way. In the future, when green chemistry is practiced by all chemists and all chemical-related companies, the term "green chemistry" will ideally disappear as all chemistry becomes green. SEE ALSO Ibuprofen; Industrial Chemistry, Organic; Solution Chemistry.

Michael C. Cann

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Guanine *See Nucleotide.*

h

Haber, Fritz

GERMAN PHYSICAL CHEMIST
1868–1934

Fritz Haber, born in Breslau, Prussia (now Wroclaw, Poland), successfully applied physical chemistry to technological problems. In 1918 he won the Nobel Prize in chemistry for his **synthesis** of ammonia from the elements, an important starting material in the production of fertilizers and explosives.

synthesis: combination of starting materials to form a desired product

Haber, whose father was a natural dyestuff importer, was destined to enter the family business at a time when synthetic dyes began to dominate the market, and his fortunes soon floundered. In 1894 the young Haber became assistant to Hans Bunte at the Technical University of Karlsruhe. Self-taught in physical and electrochemistry, he applied these new theories with impressive results to chemical technology, particularly to the **combustion** of hydrocarbons, the electrolysis of salts, and the fixation of nitrogen. In 1906 he was appointed professor at Karlsruhe, but he left six years later to become director of the new Kaiser Wilhelm Institute for Physical Chemistry in Berlin. During World War I, that institute was transformed into Germany's headquarters for chemical weapons research and production, with Haber remaining as its director. When the Nazis in 1933 began to dismiss all Jews from civil service, Haber, himself a Jew who had converted to Christianity, immediately resigned and emigrated to Great Britain. He was

combustion: burning, the reaction with oxygen

invited to head the physical chemistry section of the new Weizmann Institute in Palestine, but died shortly before its establishment.

The most abundant component of common air, elementary nitrogen, stubbornly resists chemical reactions. However, certain bacteria can transform it to ammonia (the so-called fixation of nitrogen) as the essential raw material for protein production in plants. That was already known in the late nineteenth century when a rapidly growing population required a more efficient agriculture to be supported by fertilizers including "fixed nitrogen." At that time natural niter (KNO_3), or guano from Chile, was virtually the only nitrogen source for fertilizers, so chemists were challenged to find ways to fix nitrogen from the air. In the early 1900s, several prominent physical chemists, including Henri-Louis Le Châtelier, Friedrich Wilhelm Ostwald, and Walther Hermann Nernst, were experimentally and theoretically working on this issue from two different approaches to nitrogen: **oxidation** to nitrogen oxide and reduction with hydrogen to ammonia.

German chemist Fritz Haber, recipient of the 1918 Nobel Prize in chemistry, "for the synthesis of ammonia from its elements."

oxidation: process that involves the loss of electrons (or the addition of an oxygen atom)

equilibrium: condition in which two opposite reactions are occurring at the same speed, so that concentrations do not change

Although most researchers soon dropped the topic because of little success, from 1904 on Haber continued investigating both approaches under contract with the chemical company BASF (Badische Anilin- und Sodafabrik), who offered him money, equipment, and patent shares. The path to ammonia turned out to be more promising if the reaction rates were increased by catalysts at high temperature. Thermodynamics required low temperature, however, to move the **equilibrium** toward higher yields of ammonia. Because thermodynamics predicted the same effect at high pressure, Haber and his coworkers at BASF searched for temperature and pressure conditions that a reaction vessel could withstand and that resulted in acceptable yields. Success came only when they found more effective catalysts, at first with osmium and uranium. In addition, they pushed the equilibrium to the product side by continuously drawing off ammonia from the reaction mixture and continuously providing new reactants, resulting in 1909 in a steady flow reactor at about 100 atm and 500°C (932°F) with ammonia yields of some 10 percent.

Haber demonstrated that the production of ammonia from the elements was feasible in the laboratory, but it was up to Carl Bosch, a chemist and engineer at BASF, to transform the process into large-scale production. The industrial converter that Bosch and his coworkers created was completely revised, including a cheaper and more effective **catalyst** based on extensive studies in high-pressure **catalytic** reactions. This approach led to Bosch receiving the Nobel Prize in chemistry in 1931, and the production of multimillion tons of fertilizer per year worldwide. SEE ALSO AGRICULTURAL CHEMISTRY; CATALYSIS AND CATALYSTS; EQUILIBRIUM; LE CHÂTELIER, HENRI; NERNST, WALTHER HERMANN; OSTWALD, FRIEDRICH WILHELM.

catalyst: substance that aids in a reaction while retaining its own chemical identity

catalysis: the action or effect of a substance in increasing the rate of a reaction without itself being converted

Joachim Schummer

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72
Hf
HAFNIUM
178.49

Hafnium

MELTING POINT: 2,150.0°C
BOILING POINT: 5,400.0°C
DENSITY: $13.31 g/cm^3$
MOST COMMON IONS: Hf^{4+}

Hafnium was discovered in 1923 by Danish chemist Dirk Coster working together with Hungarian physicist György K. Hevesy. The electronic structure of hafnium had been predicted by Niels Bohr, and Coster and Hevesy found evidence of a substance whose pattern matched what had been predicted. The element predicted by Bohr was finally identified as being part of the mineral zircon by means of x-ray spectroscopy analysis. Due to its discovery in Copenhagen (whose ancient Latin name was Hafnia), the element was named hafnium.

Most zirconium-containing minerals are 1 to 3 percent hafnium. Hafnium is a ductile metal with a brilliant silver luster. The properties of hafnium are often difficult to ascertain, as measurements of these properties are sometimes distorted by the presence of zirconium impurities. Of all the elements, zirconium and hafnium are two of the most difficult to separate from one another. Hafnium is a group IV transition element.

Because hafnium has a high absorption cross-section for thermal neutrons (almost 600 times that of zirconium), has excellent mechanical properties, and is extremely corrosion resistant, it is used to make the control rods of nuclear reactors. It is also applied in vacuum lines as a "getter"—a material that combines with and removes trace gases from vacuum tubes. Hafnium has been used as an alloying agent for iron, titanium, niobium, and other metals. Finely divided hafnium is pyrophoric and can ignite spontaneously in air.

Melting near 3,890°C, (7,034°F), hafnium carbide (HfC) has the highest melting point of any known binary compound. Hafnium nitride (HfN) also has a very high melting point (around 3,305°C, or 5,981°F). Other hafnium compounds include hafnium tetrachloride ($HfCl_4$), hafnium tetrafluoride (HfF_4), and hafnium dioxide (HfO_2). SEE ALSO BOHR, NIELS; INORGANIC CHEMISTRY; ZIRCONIUM.

Herbert W. Roesky

Hair Dyes and Hair Treatments

Hair has no vital function in the human body but provides an outward sign of health and social communication. The history of hair coloring dates from ancient dynasties of Egypt and China where mineral and plant dyes were widely available to cosmeticians. Through the ages, women in particular have dyed their hair to hide grayness and to improve their appearance.

General Features of Hair

In all mammals, hair develops as an epidermal structure from papillae deep in the skin and acquires characteristic patterns on the scalp, eyebrows, eyelashes, and elsewhere on the body. In humans, hair growth is continuous throughout life (declining with advancing age), occurs in cyclic patterns, and

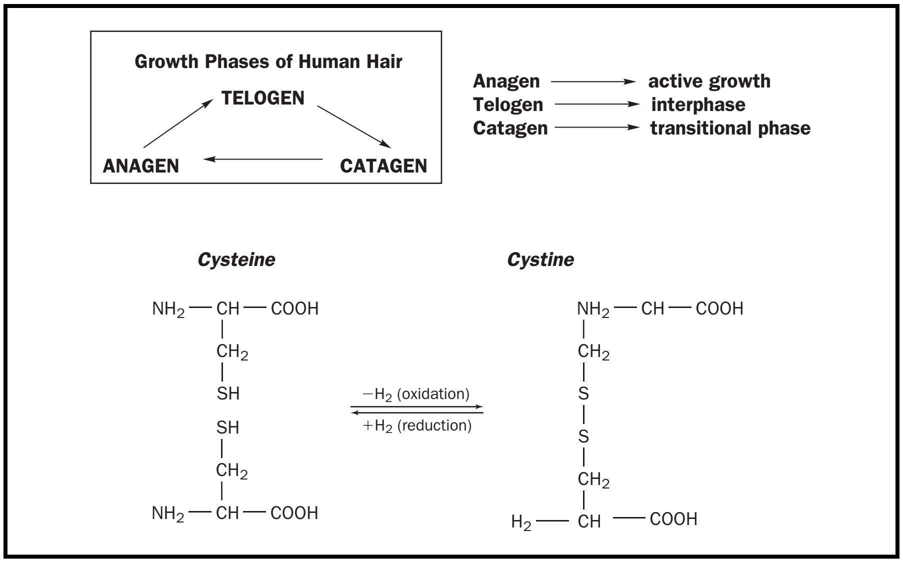

Figure 1.

is influenced by **androgens**, thyroid hormones, and dietary factors. Human hair is composed largely of keratin and consists of a narrow central medulla surrounded by a thick envelope (cortex) of elongate cells, which contain numerous melanin granules that determine the natural color. The hair is ensheathed in a multilayered cuticle of overlapping cells that become progressively imbricated (having edges overlapping in a regular arrangement) with continued growth. These cuticular cells are rich in cystine (**disulfide bonds**) and become rough or show a weathered appearance through exposure to environmental exposure or poor health.

androgen: group of steroids that act as male sex hormones

disulfide bond: two bonding sulfur atoms, –S–S–

Chemically, human hair contains approximately 85 percent protein, 7 percent water, 3 percent **lipid**, 4.7 percent protein-bound sulfur (as cystine), and low concentrations of trace minerals (e.g., iron, zinc, copper). The phosphorus content is approximately 80 milligrams per 100 grams (0.003 ounces per 3.5 ounces) of hair. Hair is normally associated with sebum and exocrine secretions from skin glands that confer greasiness but influence its water content and mechanical and physical properties.

lipid: a nonpolar organic molecule; fatlike; one of a large variety of nonpolar hydrophobic (water-hating) molecules that are insoluble in water

Hair follicles are determined prenatally; about 100,000 hairs are found on the scalp region of most adults. Hair density, color, and condition vary according to age, race, and genetic background. Natural hair colors vary from albino or white to blond, red, or intense black and reflect ethnic origin (Caucasoid, Negroid, etc.), age, diet, and health. While hair color is closely related to the density of melanin granules, impairment in a person's health or substances in the diet that influence the availability of trace minerals are potential causes of changes in hair color or condition. The configuration of the hair shaft (i.e., straight, wavy, spiral, or peppercorn) is attributable to the number and distribution of disulfide bonds. Hair straightening requires reduction of these disulfide bonds and fiber cross-linkages.

Hair serves to eliminate toxic materials (e.g., lead) and **metabolites** from the body, and may be used to monitor environmental contamination. For example, copper deficiency is a cause of Menke's "kinky" hair syndrome; protein deficiency leads to hair loss and discoloration. Hair keratin carries a strong negative charge and binds inorganic materials; it becomes prone to

metabolites: products of biological activity that are important in metabolism

discoloration through exposure to environmental chemicals (e.g., cobalt, tar in cigarettes, picric acid, trinitrotoluene, etc.). Prolonged exposure to copper in diet, tap water, or swimming pools is a cause of green hair.

Natural Hair Color and Its Control

tyrosine: one of the common amino acids

oxidation: process that involves the loss of electrons (or the addition of an oxygen atom)

Melanin granules are secreted by melanocytes in the hair papilla and distributed to keratin in the hair cortex and inner layers of the hair sheath during normal development. Melanogenesis is subject to hormonal control and has been the focus of intensive genetic studies. Two main forms of melanin exist in human skin—eumelanin and phaeomelanin, both of which are derived from **tyrosine** through the action of tyrosinase (a cupro-enzyme) and possibly other key enzymes (with nickel, chromium, iron, and manganese as cofactors). Tyrosine is converted to dihydroxyphenylalanine and, via a series of intermediate steps, to indole-5,6-quinone, which polymerizes to eumelanin. Phaeomelanins are produced by a similar mechanism but with the incorporation of sulfur (as cysteine) by a nonenzymatic step in the **oxidation** process.

Hair color is a balance between these two melanins. Albino or white-haired individuals have latent melanocytes, but possibly show defects in tyrosinase-mediated events. Graying of the hair is age-related and possibly results from declining melanocytic function or retarded hair growth resulting from atrophy or degenerative changes in hair papillae. Hair melanin absorbs insufficient ultraviolet (UV) light energy to afford protection for most individuals against sunburn.

Hair Dyes and Cosmetic Coloring

A wide variety of dyes, dressings, and conditioners are available to men and women to enhance the color of hair or to alter its condition, providing the “feel good” factor. Natural hair dyes such as henna and mineral salts are still used, but hair dyeing increasingly involves careful chemical manipulation of the chemistry of hair fibers through bleaching or enhancement of natural colors. Additionally, social and cultural customs have led to the increasing demand for exotic colors (reds, greens, blues, yellows, etc.). Hair coloring is a well-defined science with intense study of the interaction between hair keratin and highly reactive organic dyes, oxidizing agents, and conditioners.

Available hair dyes include:

- Minerals such as lead acetate (<1% aqueous), lead sulfide (kohl); silver nitrate; salts of bismuth, copper, and cobalt (commonly called “gradual” colorants)
- Vegetable materials such as henna (flowers and leaves of *Lawsonia inermis* that contain acidic naphthoquinone, chamomile, and indigo)
- Synthetic dyes including a large number of organic dyes to provide permanent, semipermanent, temporary, or progressive color changes or to enhance natural colors

The dyeing process provides for temporary, semipermanent (direct dyes), and oxidation-type reactions (semipermanent or permanent colors). It may involve absorption or adsorption (electrostatic) of the colorant into/to the hair structure, bleaching or otherwise masking the natural melanin col-

Table 1.

COLOR INDEXED DYES USED AS TEMPORARY COLORS IN HAIR COSMETICS

CI Acid Yellow 1	
CI Acid Yellow 3	(D & C Yellow No.10)*
CI Acid Orange 7	(D & C Orange No. 4)
CI Acid Orange 87	
CI Acid Red 3	(D & C Red No. 33)
CI Acid Red 211	
CI Acid Violet 43	(D & C Violet No. 2)
CI Acid Violet 73	
CI Acid Blue 9	(FD & C Blue No. 1)
CI Acid Blue 168	
CI Acid Green 25	(D & C Green No. 5)
CI Acid Brown 19	
CI Acid Brown 45	
CI Acid Black 107	
CI Basic Yellow 57	(Arianor™ Straw Yellow)
CI Basic Red 76	(Arianor™ Madder Red)
CI Basic Blue 99	(Arianor™ Steel Blue
CI Basic Brown 16	(Arianor™ Mahogany)
CI Basic Brown 17	(Arianor™Sienna Brown)
Sunset Yellow	(FD & C Yellow No. 6)
Ponceau Red	(FD & C Red No. 4)
CI Solvent Brown 44	

*F - food color, D - drug additive, C- cosmetic coloring

ors, or alteration of the structure of the hair shaft, allowing deep penetration of the colorant. The hair cuticle provides a barrier to the absorption of hair dyes, particularly those of high molecular weight, but damaged fibers exhibiting higher negative charges and reduced phospholipid content are more porous. Dye uptake is determined by the partition coefficient between the hair and the dye carrier (water, alcohol, etc.), pH, and chemical charge (dye-fiber interaction). Thickeners and **surfactants** can also influence dye uptake.

surfactants: surface-active agents that lower the surface tension of water; e.g., detergents, wetting agents

The vast array of natural dyestuffs, metallic salts, and synthetic organic chemicals available to cosmeticians are regulated in the United States (by the Food and Drug Administration [FDA]), the European Union, and many other countries, and regulatory toxicity information is documented.

Henna. Henna is the oldest and most widely used vegetable dye utilized in hair coloring. A temporary chestnut color is produced in blond or auburn hair by applying a paste of henna flowers and leaves ground in hot water immediately before use. (The dye is unstable in **aqueous solution**.) The addition of indigo achieves darker blue-black shades; extracts of walnut shell or logwood enhance brown coloration.

aqueous solution: homogenous mixture in which water is the solvent (primary component)

Mineral dyes. Of the mineral dyes, only lead acetate is commercially available. In the United States, the FDA permits maximal concentrations of 0.6

Table 2.

NATURAL DYES FROM PLANTS USED AS HAIR COLORANTS

Plant	Hair Colorant
Henna (*Lawsonia inermis*)	2-hydroxy-1,4-naphthaquinone
Chamomile	4',5,7trihydroxyflavone
Indigo (*Indogofera* sp.)	CI Pigment Blue 66 - $C_{16}H_{10}N_2O_2$
Logwood - haematein	$C_{16}H_{12}O_6$

Hair dyes and other hair treatments have been popular for centuries, but in recent years have been more chemically sophisticated, taking into account the chemical makeup of hair.

percent; in the United Kingdom, less than 1 percent is allowed. (Kohl or "suma," an eyelash and eyelid cosmetic used in Asian countries, contains up to 80 percent lead and is a known cause of anemia.) In contact with hair, the lead salt is poorly absorbed but interacts with keratin to deposit lead sulfide (at permitted levels [$<0.5\%$] lead is absorbed into the skin without toxic implications). Silver nitrate has been used to color hair brown-black without significant absorption of metal into the circulation; silver is deposited in the hair cortex as silver sulfide. Metallic hair dyes tend to be long-lasting and are lost as hair grows and is shed naturally. Hair coloration is achieved as a gradual process through repeated application of rinses or pastes over several days.

Temporary dyes. Temporary dyes are frequently acidic and provide short-term coloration (i.e., wash out after one shampoo). They are of low penetration and do not involve melanin bleaching or structural changes in the hair fiber. They are commonly identified with a color index (CI) number or as U.S. Certified Colors; they are water-soluble, high-molecular-weight pigments. Temporary dyes are employed in water-thin color rinses, colored hair-setting lotions, colored styling gels, lotions, and shampoos. Hair dyeing is improved when the colors are applied under moderate heat. Hair dyeing and color balance is difficult to control with temporary methods because of the inconsistency of dye delivery systems and instability of the dye-keratin "bonding."

Semipermanent dyes. Semipermanent dyeing systems are designed to last for several weeks. They impart darker colors without the use of oxidizing agents or structural changes in the hair shaft or papillae. Melanin may be partly masked but is not bleached. These dyes diffuse more readily into and out of the hair (aided by solvents and surfactants) and are progressively lost with hair shampooing and normal growth. The method employs dyes that

ESSENTIAL INGREDIENTS OF OXIDATIVE PERMANENT AND SEMIPERMANENT DYEING SYSTEMS

- Surfactant
- Solvent
- Alkalizing Agent
- Oxidant
- Dye

COLORS PRODUCED IN OXIDATIVE DYEING SYSTEMS USING SOME COMMON PRIMARY INTERMEDIATES AND COUPLERS

	p-**aminophenol**	***p***-**phenylenediamine**	**N,N-*bis*-(2-hydroxyethy)-** **p-phenylenediamine**
m-aminophenol	Warm brown	Red-brown	Medium violet
Resourcinol	Yellow green	Greenish brown	Yellow-gray
2-methylresourcinol	Ash brown	Yellow brown	Gray-violet
m-phenylenediamine	Orange-yellow	Blue	Greenish-blue
5-amino-o-cresol	Orange	Purple-red	Purple
a-*naphthol*	Red-orange	Violet	Blue

Table 3.

are already colored, and in general is without the toxic risks associated with semipermanent or permanent methods, which involve de novo color production and strong oxidizing agents. When the dye is lost through shampooing, the hair resumes its natural color.

Oxidative dyes. Oxidative hair dyeing systems involve the use of more toxic **reagents**. They are multistep processes leading to semipermanent or permanent coloration, according to the extent of bleaching involved. Surfactants and solvents influence the penetration of the active constituents; alkalizing agents determine pH. The resulting hair colorations are more stable against normal wearing processes than semi permanent preparations and involve an initial oxidation reaction, a coupling reaction, and production of a color reaction with dyeing of the hair fiber. The process requires a primary intermediate, a *m*-coupler or secondary intermediate (color modifiers), and hydrogen peroxide.

reagent: chemical used to cause a specific chemical reaction

Hydrogen peroxide is commonly used as the oxidizing agent; it has the capacity to bleach melanin but it initiates the first coupling reaction and the ultimate development of the color. Initial oxidation of primary intermediates (e.g., *p*-aminophenol, *p*-phenylenediamine) by hydrogen peroxide is followed by coupling with an agent like resourcinol, phenols, *m*-aminophenols, or *m*-phenylenediamines. Further oxidation of this secondary intermediate leads to the formation of colored indamines, indolanilines, and indophenols. As a general rule, the higher the electron-donating capacity of the coupling agent (especially unsubstituted carbocyclic *m*-couplers), the higher the absorbance maximum of the indo-dye formed. In the presence of couplers, di- and monoimines react to produce indo-dyes.

Many of the organic aromatic amines used in hair dyes are strong sensitizers and oxidative dyes should be used with extreme caution. *P*-phenylenediamine and its derivatives, commonly employed in permanent or semipermanent hair colorings, are strong sensitizing agents and may damage the hair. Although a large number of possible combinations of primary intermediates and couplers leading to the production of exotic hair colors is possible, the cost of conducting regulatory toxicological evaluation is prohibitive in developing many interesting colors.

Bleaches

Lightening or removal of hair color without structurally damaging the hair shaft is a difficult process. Oxidizing agents, including hydrogen peroxide,

COMPOSITION OF TYPICAL STYLING MOUSSE

- Polyoxyethylated fatty alcohol
- Deionized water
- Polyquaternium compound
- Vinyl caprolactam/polyvinylpyrolidone/dimethylaminoethyl methacrylate copolymer
- Ethanol
- Amodimethicone—tallow trimonium chloride
- Additives (perfumes, preservatives, etc.)

can be extremely harmful to hair and will oxidize some cystine to cysteic acid, rendering the fibers less cohesive and susceptible to hydration and swelling under alkaline conditions. Bleached hair shows a loss of melanin granules at the periphery of the hair. Hair color is lost (platinum blond appearance) and the fibers become dry and fragile. Bleaching is inhibited by shampoos or acid rinses.

Hair Conditioners

Hair conditioning includes permanent waving, straightening, and setting. In each case, sequential chemical treatments lead to modifications of the hair shaft with temporary or prolonged changes in disulfide bond distribution and behavioral characteristics. Softening, reshaping, and hardening are integral to permanent waving and involve an initial reduction in disulfide bonds and adhesiveness of adjacent hairs using heat or steam, thioglycollates, or ammonium hydroxide; styling with heated rollers; and setting or neutralizing the reaction. This last event is a reversal of the earlier reduction process with reconstitution of disulfide bonds from adjacent cystine moieties using hydrogen peroxide or a similar oxidizer. Hair straightening is a similar process, but may involve the additional use of hair dressings like gels, sprays, and creams (pomades) to hold the hair in place. Hot comb techniques may be used to disrupt the disulfide bonds followed by application of oils, petroleum jelly, or liquid **paraffin**.

paraffin: saturated aliphatic hydrocarbon (alkane), or hydrocarbon wax

Mousses are designed for hair styling and setting hair in position. Commonly, formulations are based on cationic conditioning polymers with quaternary ammonium salts, alcohols, perfumes, colorants, water, and preservatives. They may be in propellant, foam, or jelly form for direct application to hair after shampoo or cutting. SEE ALSO FIBROUS PROTEIN; FORMULATION CHEMISTRY; PROTEINS.

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Hall, Charles

AMERICAN CHEMIST
1863–1914

Although aluminum is now widely used as a structural material, this was not always the case. Common in Earth's crust, aluminum is difficult to win from its ore because it is such a reactive **metal**. In the 1850s French chemists interested Napoléon III in this rare and costly metal; he considered using it for soldiers' helmets, and even reserved a set of aluminum tableware for his most honored guests. By the 1880s chemical reduction techniques had been discovered, and the price per pound dropped from over $100,000 to near $100.

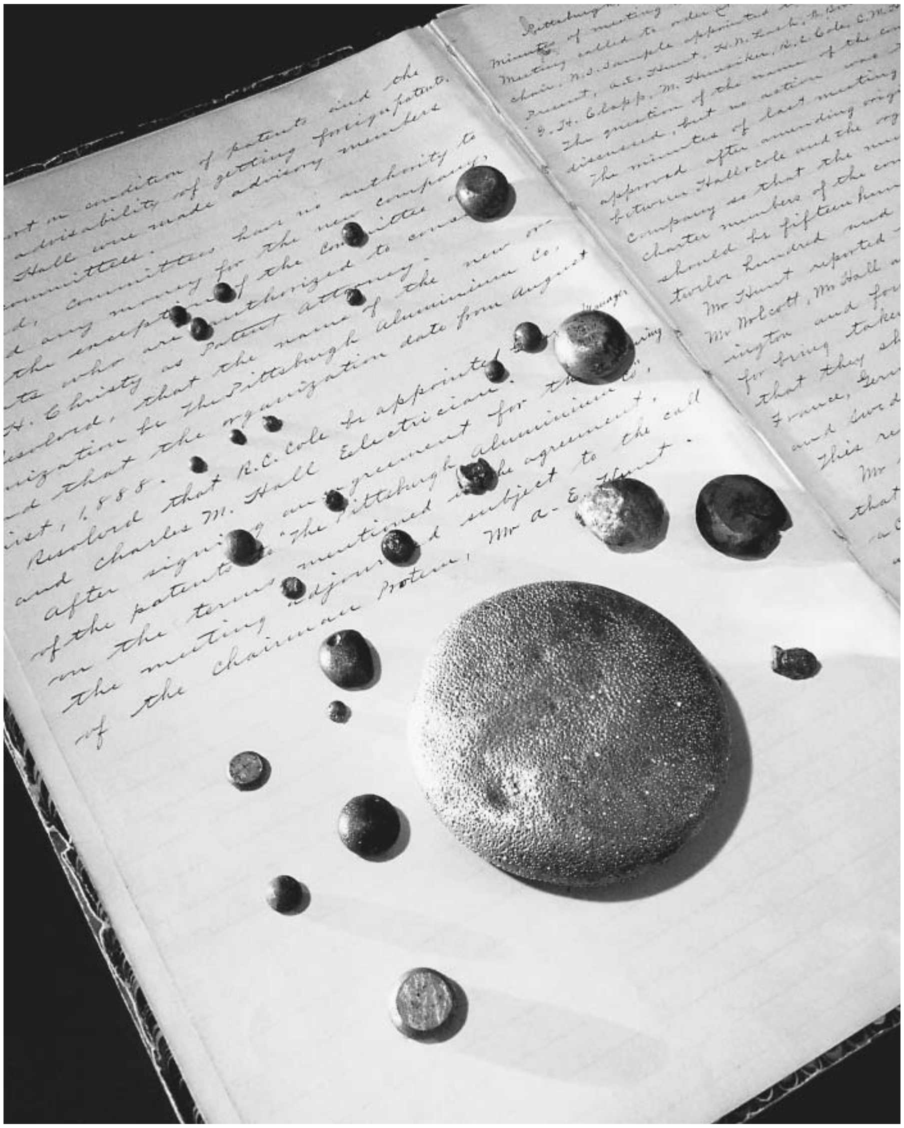
metal: element or other substance the solid phase of which is characterized by high thermal and electrical conductivities

Born in Thompson, Oregon, on December 6, 1863, Charles Martin Hall was interested in minerals since the age of twelve. While enrolled at Oberlin College in Ohio, Hall took a class from distinguished professor Frank Fanning Jewett, who had a sample of the precious metal to show the class. After a stirring lecture on the topic, he finished with, "Any person who discovers a process by which aluminum can be made on a commercial scale will bless humanity and make a fortune for himself." Inspired by such a win-win challenge, Hall reportedly said, "I'm going for that metal."

After graduating from Oberlin in June 1885, Hall continued his work in a woodshed behind his family home. There, starting with a blacksmith's forge and **galvanic** cells constructed from fruit jars, he began to investigate mixtures of aluminum and fluorine-containing minerals. Along with help from his sister (an Oberlin student) and continued guidance from Jewett, Hall discovered that alumina (Al_2O_3) and the mineral cryolite (Na_3AlF_6) fuse well and do so at a relatively low temperature (near 1,000°C [1,832°F]), compared to pure alumina. After months of work, Hall and his sister broke open their graphite crucible on February 23, 1886, to find tiny globules of a silvery metal—aluminum. Hall rushed to show them to Jewett, who confirmed his discovery. These same samples are preserved by Alcoa as the company's "crown jewels."

galvanic: relating to direct current electricity especially when produced chemically

Hall's next move in his quest to "bless humanity and make a fortune for himself" was to make aluminum production commercially feasible. Upon receiving the financial backing of local industrialists, the Pittsburgh Reduction Company was formed, and Hall and his employee Arthur Vining Davis



American chemist and inventor Charles Hall coinvented (independently) an inexpensive process for producing aluminum. This photo shows the first aluminum created by Hall in 1886.

produced the first commercial aluminum on Thanksgiving Day, 1888. There still remained complicated patent infringement cases to argue, but eventually Hall was victorious. A more serious challenge came from the independent codiscoverer of the process, Paul Héroult, a French chemist the same age as Hall performing basic research on aluminum-containing compounds. Héroult filed for a patent about the same time that Hall did, but again, Hall won the dispute over patent rights. Nevertheless, the electrolytic reduction of aluminum is rightly named the Hall-Héroult process, honoring both of its discoverers.

Once again, a chemical idea had turned industrial, as the price per pound of aluminum dropped from $4.86 in 1888 to $0.78 in 1893. In 1907 the company was reorganized as the Aluminum Company of America (Alcoa), of which Hall was made a vice-president. In 1911 Hall was awarded the Perkin Medal for his process; Héroult graciously traveled across the Atlantic to congratulate him at the ceremony. Before his death in 1914, Hall donated one-third of his fortune to a grateful Oberlin College, where today stands a life-sized statue of its benefactor, constructed entirely of aluminum. SEE ALSO ALUMINUM; INDUSTRIAL CHEMISTRY, INORGANIC.

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Halogens

The halogens are the family of chemical elements that includes fluorine (atomic symbol F), chlorine (Cl), bromine (Br), iodine (I), and astatine (At). The halogens make up Group VIIA of the Periodic Table of the elements. Elemental halogens are diatomic molecules. However, due to their high reactivity, the halogens are never found in nature in native form. The family name means "salt-forming," from the Greek for salt, *halos*, and for generating *genes*. The salinity of the oceans on Earth is due in large part to such halogen salts (halides) as sodium chloride (NaCl) and potassium iodide (KI).

Chlorine gas belongs to the halogen chemical family.

Halogens display physical and chemical properties typical of nonmetals. They have relatively low melting and boiling points that increase steadily down the group. Near room temperature, the halogens span all of the physical states: Fluorine and chlorine are gases, bromine is a liquid, and iodine is a solid. All of the elements are colored, with the color becoming more intense moving down the group. Fluorine gas is pale yellow, and chlorine gas is a yellowish green. Liquid bromine and its vapors are brownish red. Solid iodine appears as shiny, dark gray crystals, and the vapors are a deep purple. The halogens are poor thermal and electrical conductors in all phases, and as solids they are brittle and crumbly. The halogens have distinctive, unpleasant odors, will burn exposed flesh, and are toxic.

The neutral atoms of the halogens possess seven outer electrons. An additional electron can be added to halogen atoms to form singly charged negative ions. These ions have a closed outer-shell configuration. Electronegativity is a measure of the ability of an atom of one element to remove an electron from an atom of another element. As a group, the halogens are among the most **electronegative** elements. Fluorine has the highest electronegativity of all the elements. Halogens are so reactive that all the elements except helium and neon have been found to react with at least one of the halogens. Fluorine is always assigned a formal **oxidation** number of −1, whereas the other halogens can exhibit a range of oxidation numbers.

electronegative: capable of attracting electrons

oxidation: process that involves the loss of electrons (or the addition of an oxygen atom)

The ability of halogens to form chemical compounds with all metals and most nonmetals has led to a wide variety of uses for these elements. Chlorine is used as a bleach and a disinfectant. Iodine has been used as a topical microbicide. Iodine and bromine are added to halogen lamps to lengthen the life of the filament and prevent darkening of the bulb. Chloride and iodide are essential dietary minerals for humans. Organic compounds containing halogens are used as fire-retardants (halons), as refrigerants (Freons), and in nonstick coatings (Teflon). Silver bromide and silver iodide have been used in photographic emulsions since the early days of photography. Many halogenated compounds are toxic. A well-known example is DDT (dichlorodiphenyltrichloroethane), once a widely applied pesticide that was banned in the United States after severe environmental effects were discovered. All known **isotopes** of astatine are radioactive, with the longest-lived isotope having a half-life of about eight hours. Relatively little is known of the physical and chemical properties of astatine. However, it is predicted to have properties similar to iodine. SEE ALSO BROMINE; CHLORINE; FLUORINE; IODINE.

isotope: form of an atom that differs by the number of neutrons in the nucleus

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Heat

Heat is the transfer of energy that results from the difference in temperature between a system and its surroundings. At a molecular level, heat is the transfer of energy that makes use of or stimulates disorderly molecular motion in the surroundings. For instance, when a hydrocarbon fuel burns, the energy released in the reaction stimulates the surrounding atoms and molecules into more vigorous random motion, and we refer to this escape of energy as heat. Heat is not stored: Heat is energy in transit.

The measurement of quantities of energy transferred as heat is called *calorimetry*. Such a measurement is commonly made by observing the rise in temperature caused by the process being studied and interpreting that rise in terms of the heat produced. Calorimetry is used to measure the changes in internal energy and enthalpy that accompany chemical reactions. The field of study is called *thermochemistry*, and it is used to assess the efficacy of fuels, the energy flow in chemical plants, and the strengths of chemical bonds. Measurements of the heat produced or absorbed by chemical reactions are central to thermodynamics, and to assessments of whether or not a particular reaction will tend to occur.

In thermodynamics, the quantity of energy transferred as heat as a result of a chemical reaction is identified with the change in the internal energy of the system if the transfer takes place without change in the system's volume, and with the change in enthalpy of the system if the transfer takes place at constant pressure. The energy or enthalpy change accompanying a chemical reaction that is inaccessible to measurement may be determined by using Hess's law, which states that the enthalpy change accompanying a chemical reaction can be regarded as the sum of the enthalpy changes of the reactions into which the overall reaction may be divided. Hess's law is no more than a special application of the first law of thermodynamics.

The source of heat as a fuel burns is the energy released when the bonds characteristic of the reactants are replaced by the bonds characteristic of the products. Energy is released when hydrocarbons burn because of the great strengths of the oxygen–hydrogen and oxygen–carbon bonds that are formed in the products (water and carbon dioxide), replacing the relatively weak carbon–hydrogen and carbon–carbon bonds of the fuel. Ultimately, the energy of burning fuel is the energy released as the electrons and atomic nuclei settle into more favorable arrangements (just as nucleons do in the much more exothermic processes accompanying **nuclear** rearrangements).

nuclear: having to do with the nucleus of an atom

Although the term "heat energy" is commonly encountered in casual conversation, strictly speaking there is no such entity. The term is commonly used in place of the more precise term "energy of thermal motion," where thermal motion is random molecular motion, as in the motion of molecules in a gas. Nor is heat stored: Only energy is stored, and heat is one of the modes by which it may be increased or extracted. SEE ALSO CHEMISTRY AND ENERGY; ENERGY; EXPLOSIONS; TEMPERATURE; THERMOCHEMISTRY; THERMODYNAMICS.

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Heavy Metal Toxins

Even at a very low level, heavy metal ions can cause serious health effects, including reduced growth and development, cancer, organ damage, nervous system damage, and in extreme cases, death. The most common heavy metal toxins are aluminum, **arsenic**, cadmium, lead, and mercury. Once emitted from their sources, they have the property of accumulating in the environment for many years. They enter the human body through breathing, drinking, and skin absorption. They also can accumulate in the bodies of animals and humans before they even cause damage.

arsenic: toxic element of the phosphorus group

The sources of heavy metal ions are diverse and specific to each element. Aluminum is mostly found in canned food, cookware, antacids, aluminum foils, and drinking water. Arsenic is encountered through air pollution and in drinking water, meat from commercial farms, and wood preservatives. Cadmium originates mainly from cigarette smoke, air pollution, batteries, fish, paint, and food grown in cadmium-laden soil. The major sources of lead are gasoline, house paints, lead pipes, mines, and batteries. "Silver" dental fillings constitute the most important source of mercury. Other sources of mercury are from gold mining and fish. In general, the increased use of coal favors exposure to major heavy metals. What then is the mode of action of heavy metal ions?

The heavy metal ions form complexes with proteins, in which **carboxylic acid** (–COOH), amine ($–NH_2$), and thiol (–SH) groups are involved. These modified biological molecules lose their ability to function properly and

carboxylic acid: one of the characteristic groups of atoms in organic compounds that undergoes characteristic reactions, generally irrespective of where it occurs in the molecule; the $–CO_2H$ functional group result in the malfunction or death of the cells. When **metals** bind to these groups, they inactivate important enzyme systems, or affect protein structure, which is linked to the **catalytic** properties of enzymes. This type of **toxin** may also cause the formation of radicals, dangerous chemicals that cause the **oxidation** of biological molecules.

metal: element or other substance the solid phase of which is characterized by high thermal and electrical conductivities

catalysis: the action or effect of a substance in increasing the rate of a reaction without itself being converted

toxin: poisonous substance produced during bacterial growth

oxidation: process that involves the loss of electrons (or the addition of an oxygen atom)

Some diseases associated with heavy metal ions are as follows:

- Aluminum has been associated with Alzheimer's and Parkinson's disease, senility, and presenile dementia.
- Arsenic exposure can cause, among other illnesses or symptoms, cancer, abdominal pain, and skin lesions.
- Cadmium exposure produces kidney damage and **hypertension**.
- Lead and mercury may cause the development of autoimmunity, in which a person's immune system attacks its own cells. This can lead to joint diseases and ailments of the kidneys, circulatory system, and neurons. At higher doses, lead and mercury can cause irreversible brain damage.

hypertension: condition in which blood pressure is abnormally high

Heavy metal poisoning or intoxication can be diagnosed through analysis of samples from certain parts of the body. For example, lead poisoning is diagnosed by analyzing blood samples from affected individuals. The maximum allowed concentration of lead is 10 micrograms (3.5×10^{-7} ounces) per deciliter of blood. At exposures above this level, action must be taken to treat the victim.

A common treatment for metal intoxication is the use of chelators. A chelator is a flexible molecule with two or more **electronegative** groups that can form stable complexes with cationic metal atoms. The complexes are then eliminated from the body. The most widely used chelator is ethylenediaminetetraacetic acid (EDTA). It has four binding positions (two nitrogen atoms and two oxygen atoms) that focus on the metal ion. It works very well on many metals, the most notable being calcium, magnesium, and lead. SEE ALSO ENZYMES; PROTEINS; TERTIARY STRUCTURE; TOXICITY.

electronegative: capable of attracting electrons

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Heisenberg, Werner

GERMAN PHYSICIST
1901–1976

More so than any other physicist of the twentieth century, Werner Karl Heisenberg challenged our fundamental notions of the surrounding world. It could be argued that as the author of papers on quantum mechanics and the uncertainty principle, he nailed the coffin shut on the **deterministic Newtonian** version of the universe. Heisenberg replaced precision and accuracy with probabilities and uncertainties, and in so doing, he opened up the world of the subatomic to our understanding.

deterministic: related to the assumption that all events are based on natural laws

Newtonian: based on the physics of Isaac Newton

German physicist Werner Karl Heisenberg (fifth from left), recipient of the 1932 Nobel Prize in physics, "for the creation of quantum mechanics, the application of which has, inter alia, led to the discovery of the allotropic forms of hydrogen."

Born the second son of August and Anna Heisenberg, in Würzburg, Germany, Heisenberg demonstrated promise at an early age. At the age of nine, he entered the Maximilian Gymnasium in Munich where his maternal grandfather was headmaster. The curriculum emphasized classical languages and literature, but Heisenberg excelled in the minor subjects of mathematics and physics.

Heisenberg soon outgrew the limited curriculum; he studied Einstein's relativity on his own and taught himself calculus in order to tutor a college student for her final exams. For his final oral exams at the gymnasium, he solved the equations of projectile motion, taking into account air resistance.

His adolescence was set against the backdrop of World War I. Heisenberg participated in various youth movements and even joined a military training unit that helped to bring in the fall harvest before Germany surrendered. Food was scarce. The gymnasium was closed for long periods due to a shortage of coal. With most men serving in the military, Heisenberg and his fellow students were expected to continue their studies independently.

Heisenberg entered the University of Munich in the fall of 1920. His preparation at the gymnasium essentially earned him "junior year" status. The professor of physics at Munich, Arnold Sommerfeld, quickly recognized Heisenberg's potential, and it was not long before he was taking advanced classes. Indeed, he received his doctorate in 1923, at the young age of twenty-two, having studied with Max Born and listened to the Danish physicist Niels Bohr lecture at Göttingen.

A newly minted scientist, Heisenberg returned to Göttingen to serve as Born's assistant until the spring of 1926. It was in 1925 that he achieved his first breakthrough in quantum mechanics. In essence, Heisenberg realized that certain properties do not commute and the law of commutation does not always apply. In normal mathematics, the law of commutation says that $3 \times 2 = 2 \times 3 = 6$ and the order of multiplication does not matter. However, in matrix algebra, commutation is not necessarily observed. The order of multiplication does matter and can produce quite different results. Heisenberg's solution to the problems facing Bohr's quantum model of the atom relied on matrix algebra and provided a different approach in which discontinuities could occur. At almost the same time, Erwin Schrödinger formulated an alternate version of quantum mechanics based on waves. Both competed for center stage, and this resulted in fierce academic debate because Schrödinger's quantum mechanics was more deterministic.

Heisenberg's response was his second major breakthrough: The uncertainty principle that places a limit on the accuracy with which certain properties can be simultaneously known. In particular, the simultaneous measurement of both the position and the momentum of a particle can be known only to $h/4\pi$ (with h as Planck's constant). One can measure the position of a particle to an infinite level of precision, but then its momentum has an infinite uncertainty and vice versa. This sets an absolute limit on human knowledge of the physical world and leads to the idea of **quantum mechanical** probability.

quantum mechanics: theoretical model to describe atoms and molecules by wave functions

Heisenberg went on to say: "If one wants to be clear about what is meant by the 'position of an object,' for example, of an electron . . . , then one has to specify definite experiments by which the 'position of an electron' can be measured; otherwise this term has no meaning at all" (Cassidy, "Werner Heisenberg [1901–1976]"). In effect, reality does not exist until measured. This concept not only reformulated physics, but also had a major impact on Western philosophy.

theoretical physics: branch of physics dealing with the theories and concepts of matter, especially at the atomic and subatomic levels

Heisenberg received, among many other honors, the Nobel Prize in physics in 1932 for his formulation of quantum mechanics and its prediction of observable experimental facts. His work in all aspects of **theoretical physics** kept Heisenberg at the forefront of modern physics until he died of cancer in 1976. SEE ALSO Bohr, Niels; Quantum Chemistry; Schrödinger, Erwin.

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Helium

MELTING POINT: **−272.2°C—does not solidify under its own vapor**
BOILING POINT: **−268.93°C**
DENSITY: **0.1785 g/L**
MOST COMMON IONS: **None**

2
He
HELIUM
4.0026

Helium, a colorless gas at room temperature, is the first element in the **noble gas** group, and forms few compounds. It is rare in the atmosphere (1 part in 200,000) and recovered on Earth principally by its separation from natural gas obtained in underground wells. Named for the Sun (in Greek, *helios*), helium is a component of the production of energy as well as the basis of the science and technology of cryogenics. Its presence at the surface of the Sun was first confirmed by amateur British astronomer Joseph Norman Lockyer (1868), who observed characteristic lines in the optical spectrum of the Sun, at whose surface helium is produced via theenergy-releasing fusion of hydrogen and deuterium nuclei.

noble gas: element characterized by inert nature; located in the rightmost column in the Periodic Table

Because it is such a light, nonreactive element, helium condenses (at atmospheric pressure) only at 4.2 kelvins. Furthermore, because of **quantum mechanical** effects, helium solidifies (under the application of 25.3 bars of external pressure) only at the lowest temperatures. Liquefied in large compression refrigerators, helium is used to cool cryogenic equipment, in particular the superconducting magnets used in medical magnetic resonance imaging (MRI). At 2.17 kelvins liquid helium transforms into an unusual quantum **phase**, called a superfluid, which has no viscosity and exhibits bizarre flow properties, such as its creeping out of containers.

quantum mechanics: theoretical model to describe atoms and molecules by wave functions

phase: homogeneous state of matter

The gas is also used to fill balloons, in gas discharge lamps, and as an additive in the breathing gases of astronauts and scuba divers. The rarer stable **isotope** of helium (^{3}He) is produced by the decay of radioactive tritium, and is used in resonance imaging and in the attainment of very low temperatures, about 0.010 kelvin, via a process known as dilution refrigeration. SEE ALSO Noble Gases; Nuclear Fusion.

isotope: form of an atom that differs by the number of neutrons in the nucleus

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Hemoglobin

Hemoglobin is an iron-containing protein found in the blood of nearly all vertebrates and many **invertebrates**. It transports oxygen from the lungs or gills of an animal to the tissues. Four **polypeptide** chains, each wrapped in a specific way around its own **heme group**, make up the hemoglobin molecule. An iron atom in the **ferrous** state (Fe^{2+}) sits in the middle of the heme. **Ferric** hemoglobin (Fe^{3+}) cannot bind oxygen.

invertebrate: category of animal that has no internal skeleton

polypeptide: compound containing two or more amide units—C(O)NH—produced by the condensation of two or more amino acids

heme group: functional group formed by an iron atom interacting with a heterocyclic ligand called a porphyrin

ferrous: older name for iron in the +2 oxidation state

ferric: older name for iron in the +3 oxidation state

The polypeptide chains of hemoglobin are of two kinds; in the hemoglobin of an adult human, HbA, they are designated as α and β, and the subunit structure of HbA is written $\alpha_2\beta_2$. The α chain contains 141 amino acid residues, the β chain 146. Throughout most of the animal kingdom the subunit structure of hemoglobin remains the same: two polypeptides of one kind with 141 amino acid residues and two of another with 146 residues. The amino acid sequences (the primary structure) of the polypeptides, however, are species dependent. Closely related animals display fewer differences in these amino acid sequences. The α and β chains of human hemoglobin, for example, differ from chicken hemoglobin in 35 and 45 places, respectively. Between human and horse α and β chains these differences drop to 18 and 25. As for chimpanzee and human, their hemoglobins are identical.

Often several kinds of hemoglobin exist in a given animal. In the adult human, for example, HbA ($\alpha_2\beta_2$) makes up 98 percent of the total hemoglobin, and HbA_2 ($\alpha_2\delta_2$), the remaining 2 percent. The polypeptide chain δ has the same number of amino acids as the β chain, but the sequences differ in 10 places. A third kind of human hemoglobin, fetal hemoglobin or HbF ($\alpha_2\gamma_2$), constitutes over 80 percent of the total hemoglobin of a newborn, but vanishes rapidly during the first year of life. The amino acid sequences of the γ and β chains differ in 39 of the 146 residues. Additional types of human hemoglobins exist at embryonic stages of life.

Each polypeptide chain of a hemoglobin molecule coils into several helical segments (the secondary structure of the polypeptide chain) that are linked with nonhelical segments. Intertwining sets of helices wrap tightly around the heme group and produce a compact subunit (the tertiary structure). The four subunits are packed into a nearly spherical package (the quaternary structure) of 55-angstrom (2.17×10^{-7}-inch) diameter.

Each ferrous iron within hemoglobin provides one binding site for O_2. Thus a single hemoglobin molecule has the capacity to combine with four molecules of oxygen. Hemoglobin binds oxygen in a cooperative fashion; occupation of one binding site enhances the affinity of another binding site for oxygen in the molecule. Consequently, the oxygenation curve of hemoglobin (see Figure 1), in which the fractional saturation of hemoglobin with oxygen is displayed as a function of the oxygen pressure in the alveoli of the lungs, rises slowly at first, then more steeply, until it levels off and approaches unity (100% saturation). The steep rise in the oxygenation curve over a relatively small interval of oxygen pressure allows hemoglobin to serve as an efficient transporter of oxygen. SEE ALSO Primary Structure; Quaternary Structure; Secondary Structure; Tertiary Structure; Transport Protein.

N. M. Senozan

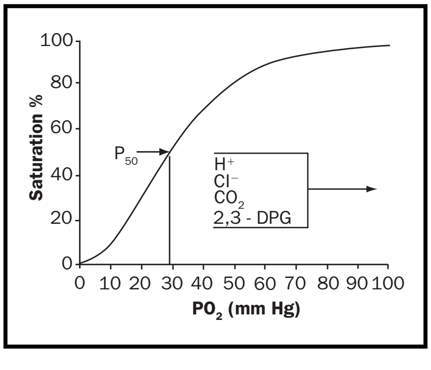

Figure 1. Hemoglobin-oxygen binding curve.

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Herbicides

Herbicides are chemicals used to destroy unwanted plants (terrestrial or aquatic) called weeds. Herbicides fall into two broad categories: inorganic (e.g., copper sulfate, sodium chlorate, and sodium arsenite) and organic (e.g., chlorophenoxy compounds, dinitrophenols, bipyridyl compounds, carbamates, and amide herbicides). Historically, inorganic compounds were the first available and the first used. There has been over a long period a continuous effort to develop herbicide compounds that are more selective—that affect weeds, as opposed to desirable plants.

Historical Developments

The decade 1890 to 1900 saw the introduction of sprays for controlling broad-leaved weeds in cereal crops, and the first efforts by the U.S. Army Corps of Engineers, using sodium arsenite, to control aquatic plants in waterways. In 1925 sodium chlorate (directly applied to soil) was first used for killing weeds. The earliest importation (from France) of sodium nitrocresylate, as the first selective weed killer, was in 1934. The year 1945 witnessed the introduction of organic herbicides and the advent of 2,4-D growth regulator (2,5-dichlorophenoxyacetic acid), subsequently leading to development of 2,4,5-T (2,4,5-trichlorophenoxyacetic acid). During the years 1965 to 1970, U.S. military forces used 2,4,5-T (Silvex) and related materials as defoliants in Vietnam, without knowing that an inevitable by-product of the **synthesis** of 2,4,5-T was a toxic substance, 2,3,7,8-tetrachlorodibenzodioxin (dioxin). There is still debate over the extent of damaging effects sustained by those airmen, soldiers, and civilians who were exposed to this material. Dioxin was present at a level of about 2 ppm (mg/kg sample) in some of the samples of 2,4,5-T (called Agent Orange), but other samples contained more than 30 ppm of the by-product. Dioxin was eventually found to be highly toxic to guinea pigs (the LD_{50} value was 1 ppb, or 1 μg compound/kg of sample), which led to the labeling of dioxin as "the world's most deadly poison," an impressive, if inaccurate, title (inaccurate because of a unique sensitivity of guinea pigs and because some natural toxins are known to be more potent).

synthesis: combination of starting materials to form a desired product

The U.S. federal government's experience with 2,4,5-T demonstrates a significant principle: One must be concerned not only with the safety of the active components of commercial products, but also with the safety of by-products that may be present in those products or that may form during natural degradation. Adherence to this principle is a major and costly challenge to those who develop herbicides, and concern for safety is partly responsible for the (at present) decreasing number of herbicides that are available for treating aquatic weeds.

It is thought that the first water hyacinths were introduced into the United States during an 1884 horticultural exposition in New Orleans, in

Herbicides are being sprayed on this California roadside.

the course of which these plants, imported from Argentina, were given away as souvenirs. It is suspected that they were accidentally put into the St. Johns River in Florida and that they, shortly thereafter, multiplied. The plant grows (under optimal conditions) at the rate of 1.8 daughter plants per parent plant per week, and rapid growth generated dense mats that affected the navigation of boats on this river and others. In 1898 the U.S. Army Corps was given responsibility for maintaining the navigability of rivers, and aquatic plant control became its responsibility as well—a responsibility that has persisted to this day.

Herbicide Toxicity

Because plants and mammals differ in organization and physiology, it might be expected that herbicides would constitute only a slight chemical hazard to mammals. Whereas some herbicides have very low toxicities in mammals, others have considerable. A number of test species are used to appraise toxicity, and their sensitivities are graded as acute (short-term) LD_{50} values.

LD_{50} refers to the amount (LD or lethal dose) that will elicit the deaths of 50 percent of the test species. It is typically expressed as the weight of herbicide per kilogram of body weight. The smaller the LD value, the greater the toxicity.

The chlorophenoxy compounds 2,4-dichlorophenoxyacetic acid (2,4-D) and 2,4,5-trichlorophenoxyacetic acid (2,4,5-T) may be the most familiar herbicides. They have been used in agriculture (to eradicate broadleaf weeds) and to control woody plants in ditches and along highways. They act as growth hormones in many plants, and can evoke active plant growth in areas in which abnormal, twisted, or curtailed growth occurs. Massive doses

CHARACTERISTICS OF REPRESENTATIVE HERBICIDES

Herbicide (type)	Control/Purpose	Acute Toxicity LD_{50} mg/kg
2,4-D (2,4-dichlorophenoxy acetic acid)	Systematic herbicide	300–1,000: rats, guinea pigs, rabbits
Acetochlor	Control of most annual grasses, some broadleaf weeds. Tolerant crops include corn, soybeans, peanuts, sugarcane.	2,953: rat acute oral
Amitrole (triazine)	Broadleaf weeds and grasses in noncrop areas, generally low toxicity.	>5,000: male rats
Arsenic acid (inorganic)	Desiccation of cotton which is to be stripped	48: young rat 100: older rats
Atrazine	Widely used selective herbicide for broadleaf and grassy weeds.	no ill effects in rats, dogs with diet of 25 ppm
Dinosep (dinitrophenol)	Control of seedlings, not established perennial weeds except with repeat treatments. Applicable to variety of crops, except cruciferous crops.	58: rats
Diquat (dipyridyl)	General aquatic herbicide; preharvest top killer or desiccant.	230: rats
Diuron (carbamate)	Low rates—broadleaf and grass weeds in cotton, sugarcane etc. general weedkiller at higher rates	3,400: oral rats
Glyphosate	Broad-spectrum herbicide Used in crop, noncrop, weed control	(Rabbit acute dermal, >5,000 mg/kg)
Metolachlor	Selective herbicide used to control annual grassweeds, yellow nutsedge, some broadleaf in corn, cotton, peanuts, and other crops	2,780: rat acute oral
Paraquat (dipyridyl)	Weed control during establishment of grass seed crops	138: male rats
Propanil (aromatic amide)	Grasses and broadleaf weeds in certain wheat crops (north) and rice (south)	1,870: rats

SOURCE: Weed Science Society of America (1994). *Herbicide Handbook,* 7th edition. Lawrence, KS: Allen Press.

Characteristics of representative herbicides.

of either 2,4-D or 2,4,5-T cause ventricular fibrillation in mammals. Lower doses cause contact dermatitis and chloracne (a kind of severe dermatitis) in workers who have contact with 2,4,5-T (which, as noted, may be mixed with 2,3,7,8-tetrachlorodibenzodioxin, or dioxin).

Dinitrophenols (as alkali salts or aliphatic amine salts) have long been used in weed control. Human exposure to these compounds has led to nausea, gastric upset, rapid breathing, tachycardia (rapid heartbeat), cyanosis, and ultimately coma. Death or recovery occurs within 24 hours.

Paraquat and diquat are the best-known examples of bipyridyl compounds. These compounds appear to act via a free radical mechanism, competing for and depriving plants of an essential **reducing agent**. These compounds are hazardous to human beings. About 200 deaths from accidental poisoning or suicide attempt occurred in the 1960s. The fatalities showed lung, liver, and kidney damage. Paraquat tends to become concentrated in the kidney, with the accumulation of toxic amounts in the lung being secondary to kidney damage.

reducing agent: substance that causes reduction, a process during which electrons are lost (or hydrogen atoms gained)

Propanil is one of a group of amide herbicides (made from aniline treated with organic acids), and is used extensively to control weeds in rice crops. Rice itself contains an enzyme that hydrolyzes propanil to 3,4-dichloroaniline and propionic acid, and so it is resistant to the herbicide. Weeds, lacking this enzyme, are adversely affected by it. (Mammalian liver cells also have an enzyme that causes this hydrolysis.)

The effects of trace contaminants in herbicides are a major concern. For example, the use of Silvex was canceled by the U.S. Environmental Protection Agency in 1979 because the herbicide contained dioxin, a toxic. However, the Army Corps of Engineers argued against the cancellation, noting the overall U.S. waterways navigation benefits. The sum total of benefits of Silvex-based weed control were judged to correspond to approximately $40 million, and the benefit–cost ratio was about 11 to 1. Set against this must be the unknown costs of a toxic substance (dioxin), whose adverse effects are still being evaluated.

The entire world market for crop protection in 2000 was estimated to be $31 billion, and it probably will not grow significantly in the near future. Herbicides are sold as special formulations, and their use in the United States occurs only after extensive testing and governmental approval. Although new chemicals are being developed, the relatively static size of the herbicide market has resulted in a reduction in the number of agrochemical companies (through mergers and acquisitions). The number of new herbicides that will become available in the future will probably be a low one. SEE ALSO Agricultural Chemistry; Gardening; Insecticides; Pesticides.

Dean F. Martin
Barbara B. Martin

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Hess, Germain Henri

RUSSIAN CHEMIST
1802–1850

Germain Henri Hess is noted today for two fundamental principles of thermochemistry: the law of constant summation of heat (known simply as Hess's law) and the law of thermoneutrality. These discoveries were remarkable in that they were postulated without any supporting theoretical framework and took place in a field of study almost totally neglected by his contemporaries. Hess's law is of immense practical importance and is used to this day to determine heats of reaction when their direct measurements are difficult or impossible.

Hess was born on August 8, 1802, in Geneva, Switzerland. At the age of three, he moved with his family to Russia when his father, an artist, became a tutor to a rich family. Hess began his medical studies in 1822 and obtained an M.D. in 1826. While in school, he became interested in chemistry and geology, and upon graduation traveled to Stockholm, Sweden, to study with Jöns Jakob Berzelius, the most renowned chemist of the period. Although he spent barely a month in Berzelius's laboratories, Hess was strongly influenced by him in his later career, and they remained lifelong friends and correspondents. After practicing medicine in Irkutsk for two years, Hess returned to St. Petersburg, where he remained a member of the academic establishment for the remainder of his life.

Although Hess, like most of his colleagues, was involved with the discovery and analysis of new substances, he became interested in the more theoretical aspects of chemistry. His investigations into the nature of chemical affinity—why atoms are attracted to each other—led him to study the amounts of heat generated by chemical reactions. His experiments, carried out on the various hydrates of sulfuric acid, showed that the heat evolved in their formation was always the same, whether the reactions proceeded directly or stepwise through **intermediates**. Although this can be seen in hindsight as a specific example of the law of the conservation of energy, Hess developed it two years before Julius Robert von Mayer elucidated the more general principle in 1842.

intermediate: molecule, often short-lived, that occurs while a chemical reaction progresses but is not present when the reaction is complete

Hess was immediately aware of the significance of his discovery and continued his studies in the same realm. In 1842 he proposed the law of thermoneutrality, which stated that no heat is evolved by the exchange reactions of neutral salts in **aqueous solutions**. He was not able to fully explain these observations, and it was not until forty-five years later that the process of electrolytic dissociation was more completely elucidated by the Swedish physicist and chemist Svante Arrhenius.

aqueous solution: homogenous mixture in which water is the solvent (primary component)

Although his research activity diminished after these two major discoveries, Hess remained influential in the development of chemistry in Russia. His textbook *Fundamentals of Pure Chemistry* saw seven editions and remained the standard Russian text in chemistry until 1861. He remained active in teaching and mentoring younger scientists, until declining health forced his retirement in 1848. He died on December 13, 1850, at the relatively young age of forty-eight. SEE ALSO ARRHENIUS, SVANTE; BERZELIUS, JÖNS JAKOB; THERMOCHEMISTRY.

Bartow Culp

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Heyrovský, Jaroslav

CZECH PHYSICAL CHEMIST
1890–1967

Jaroslav Heyrovský was born on November 20, 1890, in Prague (then part of the Austro-Hungarian Empire), where he also died on March 27, 1967. He began studying chemistry and physics at Prague University in 1909.

Between 1910 and 1914 he studied at University College in London under William Ramsay and Frederick G. Donnan, where he earned a B.Sc. degree in 1913. Following war service in a military hospital during World War I, he earned a Ph.D. degree in Prague in 1918 and a D.Sc. degree in London in 1921. In 1922 Heyrovský was promoted to full professor and head of the Institute of Physical Chemistry at Charles University (in Prague); and in 1950 he became director of the Polarographic Institute of the Czechoslovak Academy of Sciences.

Heyrovský was the discoverer of polarography and the inventor of the polarograph, an instrument that analyzes the composition of solutions electrochemically. His discovery of polarography was a culmination of the work of other scientists in electrochemistry. Other scientists' investigations of electrolysis had demonstrated the dependence of the intensity of a current flowing through a saline solution on the **voltage** applied to electrodes immersed in the solution. They found that at certain voltages, currents began to flow and **metals** were deposited on the electrodes.

voltage: potential difference expressed in volts

metal: element or other substance the solid phase of which is characterized by high thermal and electrical conductivities

The second line of research that led to polarography was the investigation of the **interface tension** between mercury and saline solutions. Gabriel Lippmann (1845–1921) found that increasing the voltage applied to mercury in contact with a surrounding saline solution changed the mercury's surface tension in a characteristic manner, which he was able to represent as a **parabolic curve** called an electrocapillary parabola. Professor Bohumil Kučera (1874–1921), Heyrovský's teacher in Prague, made a similar investigation, for which he used a mercury-dropping electrode. The electrode consisted of a capillary tube from which mercury dripped into the solution. Kučera witnessed deviations in the shapes of the curves as he varied the voltages, and proposed that Heyrovský investigate the phenomenon.

interface tension: contractile force at the junction of two liquids

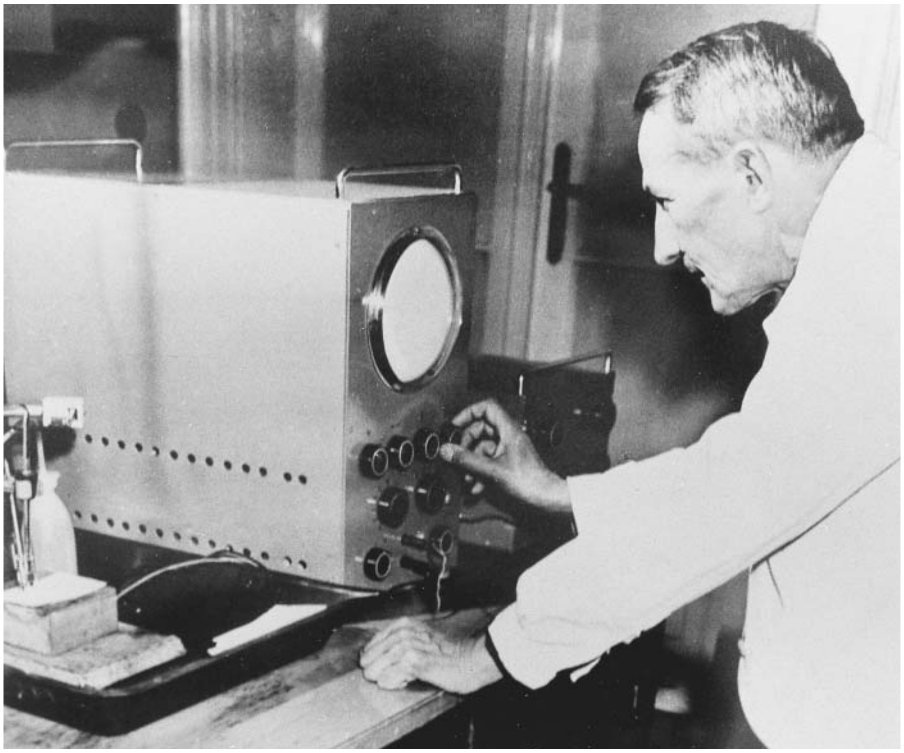
parabolic curve: planar curve each point of which is equidistant from a straight line (axis)

Heyrovský in effect combined the investigations of electrolysis and electrocapillary parabolas. In 1922 Heyrovský constructed an electrical circuit whose voltage from a battery was applied through a **Kohlrausch drum** to a mercury-dropping electrode immersed in a saline solution. The electrical potential of this electrode was then changed incrementally from 0 to 2 volts. A layer of mercury on the bottom of the vessel served as the second electrode. A mirror **galvanometer** would then detect a current flowing through this circuit, and the values of current intensity would be plotted point by point (by hand) as a function of the applied voltage. As the dissolved ions reacted electrochemically with the mercury-dropping electrode, curves with characteristic steps (polarographic waves) at certain voltage values were obtained. The identity of the ion present in the solution was determined by the voltage (expressed in electrochemical potential) at half of the height of the polarographic wave (so-called half-wave potential). The intensity of the current, represented in the graph as the height of the polarographic wave, was found to be directly proportional to the concentration of the ion.

Kohlrausch drum: rotating cylinder used to mount a variable resistance slide wire for a polarograph

galvanometer: instrument used to detect and measure the strength of an electric current

Heyrovský's method, later called polarography, became an excellent analytical tool because it yielded qualitative and quantitative analyses of a solution in a single experiment. With Masuzo Shikata (1895–1964), Heyrovský constructed the first polarograph, an instrument equipped with an electromotor that moved the Kohlrausch drum in accord with photographic paper rotating in a cylindrical cassette. It allowed the potential of the mercury-



Czech chemist Jaroslav Heyerovský, recipient of the 1959 Nobel Prize in chemistry, "for his discovery and development of the polarographic method of analysis."

dropping electrode to change continuously. Light from the mirror galvanometer entered the cassette through a narrow slit (requiring these experiments to be performed in darkness). A continuous polarographic curve appeared upon the development of the photographic paper.

The polarograph was the first fully automatic instrument used in chemistry. For decades polarography was the only precise method for the analysis of inorganic and organic compounds in solution. Polarographic analyses of human blood serum served as a tool for diagnosing cancer during the 1940s and 1950s. Modern polarographs equipped with computers use advanced techniques such as oscillopolarography and square-wave polarography. In 1959 Heyrovský was awarded the Nobel Prize in chemistry "for his discovery and development of the polarographic method of analysis." SEE ALSO ANALYTICAL CHEMISTRY; ELECTROCHEMISTRY.

Vladimir Karpenko

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British chemist Dorothy Crowfoot Hodgkin, recipient of the 1964 Nobel Prize in chemistry, "for her determinations by x-ray techniques of the structures of important biochemical substances."

Hodgkin, Dorothy

ENGLISH CHEMIST
1910–1994

The most powerful technique for determining the structure of a chemical compound is x-ray crystallography. In this technique, a beam of x rays is focused on a crystal of a compound. The diffraction pattern produced enables chemists to determine the location of atoms within the crystals and hence deduce the molecular structure. It was Dorothy Hodgkin who pushed the limits of the technique to determine the structures of some biologically important molecules, including penicillin, **vitamin** B_{12}, and insulin.

vitamins: organic molecules needed in small amounts for the normal function of the body; often used as part of an enzyme catalyzed reaction

Born in Cairo in 1910 to English parents, Hodgkin became interested in chemistry by the age of ten. At thirteen, she attempted to analyze minerals she had brought back to England from the Sudan. Excelling in high school, in 1927 she was accepted at Oxford University, from which she graduated in 1931. Despite her obvious brilliance, Hodgkin was rejected for several positions. Fortunately, the famous crystallographer John Desmond Bernal at Cambridge University agreed to take her on as a researcher.

Hodgkin enjoyed the sparkling intellectual atmosphere at Cambridge, but financial hardship forced her to take a position as a tutor back at Oxford. It was there that she began her own research career in the lonely basement of the university museum. At that time, women were not permitted to join the chemistry club at Oxford University, so she was in effect barred from sharing in the intellectual life of her colleagues.

Throughout her career, Hodgkin selected projects that were always just beyond the currently accepted limits of feasibility, her initial research on the structure of cholesterol being one such example. In 1942 Hodgkin embarked on the first groundbreaking study of her career—the molecular structure of penicillin. Penicillin was the only effective antibiotic of the time and it had to be obtained from molds. If the structure could be determined, then it would be possible to devise a method of synthesizing it in chemical factories, reducing its cost and dramatically increasing its supply. Hodgkin and her research students determined the molecular structure of penicillin in 1945, in the process devising new crystallographic techniques.

Although Hodgkin had made major contributions to science, she still held the lowly rank of tutor. Deep in debt, she asked a senior professor to help her acquire a better position. With his help, she was appointed university lecturer in 1946. In 1948 she decided to take on the determination of vitamin B_{12}'s structure. This vitamin had been shown to prevent the disease of pernicious anemia but its chemical makeup remained unknown. With ninety-three atoms other than hydrogen, most chemists regarded the task of identifying its structure as impossible. Over the next six years, Hodgkin and her students toiled over the task. Their success in 1956 was the supreme triumph of her career.

Not until 1957 was Hodgkin promoted to university reader (approximately the equivalent of a full professor in North America). Even then, she was not provided with modern lab facilities until the following year. Despite her fame, it was the **Royal Society**, not Oxford University, that offered her the pinnacle of academic success, an endowed chair. Worldwide

Royal Society: The U.K. National Academy of Science, founded in 1660 recognition of her work on the determination of the structures of biochemically important molecules came in 1964 when she was awarded the Nobel Prize in chemistry.

Hodgkin's third major project was determining the structure of the protein insulin. It was only technical advances in the 1960s that made the solution finally possible. When the results were published in 1969, the researchers were listed in alphabetical order, showing her willingness to share credit and her egalitarian attitude toward all research workers.

Hodgkin also had a very strong sense of social responsibility. After World War II, she became a member of the Science for Peace organization. Membership in this organization caused her to be denied a visa to attend a meeting in the United States during 1953. For the next twenty-seven years, to attend scientific meetings in the United States, she had to obtain a special entry permit from the U.S. attorney general. Only in 1990, when she was eighty years old, did the U.S. State Department relent and approve a visa application. Hodgkin formally retired in 1977, but she continued to be active in science until her death on July 30, 1994. SEE ALSO Cholesterol; Insulin; Penicillin.

Marelene Rayner-Canham
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Holmium

MELTING POINT: **1,461°C**
BOILING POINT: **2,720°C**
DENSITY: **8.803 g/cm^3**
MOST COMMON IONS: **Ho^{3+}**

67
Ho
HOLMIUM
164.9303

A member of the **lanthanide**, or rare earth, series of elements, holmium is a gray, somewhat shiny, soft **metal**. It is usually found in minerals containing several of the lanthanides. Because the **rare earths** all have the same outer electron shell configuration (6s^2), their chemical properties are very similar, making it difficult to separate them from one another in the minerals in which they are usually complexed. They are best separated via repeated ion-exchange purification, a process developed in the United States during the 1940s. Although several of the rare earths are used in industrial chemical processes and in metal alloying, holmium has few commercial uses.

lanthanides: a family of elements (atomic number 57 through 70) from lanthanum to lutetium having from 1 to 14 4f electrons

metal: element or other substance the solid phase of which is characterized by high thermal and electrical conductivities

rare earth elements: older name for the lanthanide series of elements, from lanthanum to lutetium

alloy: mixture of two or more elements, at least one of which is a metal

isotope: form of an atom that differs by the number of neutrons in the nucleus

nuclear: having to do with the nucleus of an atom

Holmium is easily oxidized, forms a wide variety of compounds, especially salts, and forms **alloys** with other metals. The pure metal has unusual magnetic properties that become apparent at low temperatures. In pure holmium the electron spins (which produce the magnetism) are aligned—not in parallel fashion as in iron, but in a manner such that helices are formed. Holmium has been used to make parts for magnets that produce intense magnetic fields. The **isotope** ^{165}Ho has an unusual football-shaped nucleus, which has been the focus of several important experiments investigating the nature of **nuclear** forces. In one atom the holmium electrons interact with the nucleus as if they produce a magnetic field of 740 tesla. This "hyperfine field" is one of the strongest such fields found in nature. SEE ALSO Cerium; Dysprosium; Erbium; Europium; Gadolinium; Lutetium; Neodymium; Praseodymium; Promethium; Samarium; Terbium; Thulium; Ytterbium.

David G. Haase

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Hormones ***See Estrogen; Steroids; Testosterone.***

1

H

HYDROGEN

1.0079

Hydrogen

MELTING POINT: **−259.14°C**
BOILING POINT: **−252.87°C**
DENSITY: **0.08988 g/L**
MOST COMMON IONS: **H^+, H^-**

Hydrogen was first recognized as a gaseous substance in 1766 by English chemist and physicist Henry Cavendish. The abundance of hydrogen in Earth's crust is 1,520 parts per million. The abundance of hydrogen in the universe by weight is 74 percent and by number of atoms is 90 percent. Hence, hydrogen is the major constituent of the universe. Under ordinary conditions (STP) on Earth, hydrogen is a colorless, odorless, tasteless gas that is only slightly soluble in water. It is the least dense gas known (0.08988 grams per liter at STP). Ordinary hydrogen gas (H_2) exists as diatomic molecules. It reacts with oxygen to form its major compound on Earth, water (H_2O). It also reacts with nitrogen, **halogens**, and sulfur, to form ammonia (NH_3), hydrogen monohalide compounds (e.g., HCl) and hydrogen sulfide (H_2S), respectively. It combines with several **metals** to form metal hydrides, and carbon to form a great many organic compounds.

halogen: element in the periodic family numbered VIIA (or 17 in the modern nomenclature) that includes fluorine, chlorine, bromine, iodine, and astatine

metal: element or other substance the solid phase of which is characterized by high thermal and electrical conductivities

isotope: form of an atom that differs by the number of neutrons in the nucleus

Hydrogen is a mixture of three **isotopes**: protium (^{1}H; atomic mass 1.007822); deuterium, or heavy hydrogen (^{2}H or D; atomic mass 2.0140; 1 atom of ^{2}H to every 6,700 atoms of ^{1}H); and tritium (^{3}H or T; atomic mass 3.016; has a radioactive nucleus). The fusion of protium nuclei (protons) to form helium is believed to be the major source of the Sun's energy. The extreme heat of reaction in hydrogen-oxygen burning is used in high temperature welding and melting processes. Hydrogen molecule addition reactions (hydrogenation) are widely used in industry, for example, for the hardening of animal fats or vegetable oils, for the **synthesis** of methanol

synthesis: combination of starting materials to form a desired product

from carbon monoxide, and in petroleum refining. see also Cavendish, Henry; Explosions; Gases.

Ágúst Kvaran

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Hydrolase

Hydrolases are hydrolytic enzymes, biochemical catalysts that use water to **cleave** chemical bonds, usually dividing a large molecule into two smaller molecules. Examples of common hydrolases include esterases, proteases, glycosidases, nucleosidases, and lipases.

cleave: split

Hydrolases carry out important **degradative** reactions in the body. During digestion, lipases **hydrolyze lipids** and proteases convert protein to amino acids. Hydrolases cleave large molecules into fragments used for **synthesis**, the **excretion** of waste materials, or as sources of carbon for the production of energy. In these reactions, many biopolymers are converted to monomers. Some hydrolases release energy as they act.

degradative: breaking down large molecules such as starch or protein into smaller fragments such as sugars or amino acids

hydrolyze: to react with water

lipid: a nonpolar organic molecule; fatlike; one of a large variety of nonpolar hydrophobic (water hating) molecules that are insoluble in water

synthesis: combination of starting materials to form a desired product

excrete: to eliminate or discharge from a living entity

One of the most important hydrolases is **acetylcholine** esterase (cholinesterase). Acetylcholine is a potent neurotransmitter for voluntary muscle. Nerve impulses travel along neurons to the **synaptic cleft**, where acetylcholine stored in **vesicles** is released, carrying the impulse across the synapse to the **postsynaptic neuron** and **propagating** the nerve impulse. After the nerve impulse moves on, the action of the neurotransmitter molecules must be stopped by cholinesterase, which hydrolyzes acetylcholine to choline and acetic acid. Some dangerous toxins such as the exotoxin of *Clostridium botulinum* and saxitoxin interfere with cholinesterase, and many nerve agents such as tabun and sarin act by blocking the hydrolytic action of cholinesterase. see also Enzymes; Hydrolysis.

acetylcholine: neurotransmitter with the chemical formula $C_7H_{17}NO_3$; it assists in communication between nerve cells in the brain and central nervous system

synaptic cleft: tiny space between the terminal button of one neuron and the dendrite or soma of another

vesicle: small compartment in a cell that contains a minimum of one lipid bilayer

postsynaptic neuron: receptor nerve cell

propagating: reproducing; disseminating; increasing; extending

Dan M. Sullivan

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Hydrolysis

Hydrolysis literally means reaction with water. It is a chemical process in which a molecule is cleaved into two parts by the addition of a molecule of water. One fragment of the parent molecule gains a hydrogen ion (H^+) from the additional water molecule. The other g roup collects the remaining hydroxyl group (OH^-). To illustrate this process, some examples from real life and actual living systems are discussed here.

The most common hydrolysis occurs when a salt of a weak acid or weak base (or both) is dissolved in water. Water autoionizes into negative hydroxyl ions and hydrogen ions. The salt breaks down into positive and negative ions. For example, sodium acetate dissociates in water into sodium and acetate ions. Sodium ions react very little with hydroxyl ions whereas acetate ions combine with hydrogen ions to produce neutral acetic acid, and the net result is a relative excess of hydroxyl ions, causing a basic solution.

catalyst: substance that aids in a reaction while retaining its own chemical identity

However, under normal conditions, only a few reactions between water and organic compounds occur. Generally, strong acids or bases must be added in order to achieve hydrolysis where water has no effect. The acid or base is considered a **catalyst**. They are meant to speed up the reaction, but are recovered at the end of it.

ester: organic species containing a carbon atom attached to three moieties: an O via a double bond, an O attached to another carbon atom or chain, and an H atom or C chain; the $\mathrm{R(C{=}O)OR}$ functional group

carboxylic acid: one of the characteristic groups of atoms in organic compounds that undergoes characteristic reactions, generally irrespective of where it occurs in the molecule; the $-\mathrm{CO_2H}$ functional group

Acid–base-catalyzed hydrolyses are very common; one example is the hydrolysis of amides or **esters**. Their hydrolysis occurs when the nucleophile (a nucleus-seeking agent, e.g., water or hydroxyl ion) attacks the carbon of the carbonyl group of the ester or amide. In an aqueous base, hydroxyl ions are better nucleophiles than dipoles such as water. In acid, the carbonyl group becomes protonated, and this leads to a much easier nucleophilic attack. The products for both hydrolyses are compounds with **carboxylic acid** groups.

Perhaps the oldest example of ester hydrolysis is the process called saponification. It is the hydrolysis of a triglyceride (fat) with an aqueous base such as sodium hydroxide (NaOH). During the process, glycerol, also commercially named glycerin, is formed, and the fatty acids react with the base, converting them to salts. These salts are called soaps, commonly used in households.

metabolism: the complete range of biochemical processes that take place within living organisms; comprises processes that produce complex substances from simpler components, with a consequent use of energy (anabolism), and those that break down complex food molecules, thus liberating energy (catabolism)

biosynthesis: formation of a complex molecule from simpler ones

oxidation: process that involves the loss of electrons (or the addition of an oxygen atom)

adenosine triphosphate (ATP): molecule formed by the condensation of adenine, ribose, and triphosphoric acid, HOP(O)OH–O–(O)OH–OP(O)OH–OH; it is a key compound in the mediation of energy in both plants and animals

Moreover, hydrolysis is an important process in plants and animals, the most significant example being energy **metabolism** and storage. All living cells require a continual supply of energy for two main purposes: for the **biosynthesis** of small and macromolecules, and for the active transport of ions and molecules across cell membranes. The energy derived from the **oxidation** of nutrients is not used directly but, by means of a complex and long sequence of reactions, it is channeled into a special energy-storage molecule, **adenosine triphosphate (ATP)**.

synthesis: combination of starting materials to form a desired product

The ATP molecule contains pyrophosphate linkages (bonds formed when two phosphate units are combined together) that release energy when needed. ATP can be hydrolyzed in two ways: the removal of terminal phosphate to form adenosine diphosphate (ADP) and inorganic phosphate, or the removal of a terminal diphosphate to yield adenosine monophosphate (AMP) and pyrophosphate. The latter is usually cleaved further to yield two phosphates. This results in biosynthesis reactions, which do not occur alone, that can be driven in the direction of **synthesis** when the phosphate bonds are hydrolyzed.

catalysis: the action or effect of a substance in increasing the rate of a reaction without itself being consumed

In addition, in living systems, most biochemical reactions, including ATP hydrolysis, take place during the **catalysis** of enzymes. The catalytic action of enzymes allows the hydrolysis of proteins, fats, oils, and carbohydrates. As an example, one may consider proteases, enzymes that aid digestion by hydrolyzing peptide bonds in proteins. They catalyze the hydrolysis of interior peptide bonds in peptide chains, as opposed to exopeptidases, another class of enzymes, that catalyze the hydrolysis of terminal peptide bonds, liberating one free amino acid at a time.

However, proteases do not catalyze the hydrolysis of all kinds of proteins. Their action is stereo-selective: Only proteins with a certain tertiary structure will be targeted. The reason is that some kind of orienting force is needed to place the amide group in the proper position for catalysis. The necessary contacts between an enzyme and its substrates (proteins) are created because the enzyme folds in such a way as to form a crevice into which the substrate fits; the crevice also contains the catalytic groups. Therefore, proteins that do not fit into the crevice will not be hydrolyzed. This specificity preserves the integrity of other proteins such as hormones, and therefore the biological system continues to function normally. SEE ALSO ENZYMES; TERTIARY STRUCTURE.

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Ibuprofen

Ibuprofen is a well-known drug that possesses **analgesic** (pain-relieving) and antipyretic (fever-reducing) properties. It is particularly known for its use in pain relief from arthritis. Ibuprofen was discovered by Dr. Stewart Adams and his colleagues in the United Kingdom in the 1950s, patented in 1961, and first made available in 1969. It became available in the United States in 1974. Ibuprofen tablets are sold under the trade names Advil and Motrin. The chemical name of ibuprofen is 2-(4-isobutylphenyl)propanoic acid.

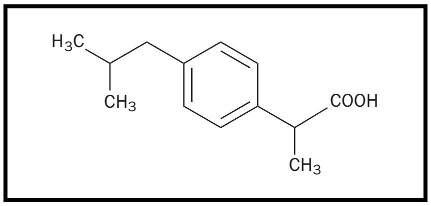
analgesic: compound that relieves pain, e.g., aspirin

Ibuprofen also has anti-inflammatory properties, and it belongs to a class of therapeutic agents known as nonsteroidal anti-inflammatory drugs, or NSAIDs. Like acetylsalicylic acid (aspirin), another NSAID, and acetaminophen, ibuprofen works by inhibiting the activity of a class of enzymes called cyclooxygenases (COX). These enzymes are significant because they catalyze the **synthesis** of prostaglandins, molecules that have both positive and negative effects in the body. Prostaglandins are, for example, protective against the development of stomach ulcers, but they can also **mediate** inflammation (as well as the pain response).

synthesis: combination of starting materials to form a desired product

mediate: to act as an intermediary agent

One of the most interesting things about human COX enzymes is that there is more than one of them—definitely two, and probably at least three. This is important to our understanding of the therapeutic effects of ibuprofen, aspirin, and acetaminophen. It had long been suspected that there was more than one COX enzyme, but it was not until 1991 that evidence for the existence of two forms, COX-1 and COX-2, materialized. It was then recognized that COX-1 is present at near constant levels in the body under all conditions (that is, it is a constitutive enzyme), whereas the levels of COX-2 could increase in response to inflammatory conditions (i.e., it is an inducible enzyme). This led to the idea that the side effects of ibuprofen and aspirin (including stomach ulcers) probably arose from inhibition of the constitutive COX-1 enzyme, whereas the therapeutic benefits arose from inhibition of the inducible COX-2 enzyme.



Structure of ibuprofen.

Ibuprofen and aspirin both inhibit COX-1 and COX-2, but they do it in different ways. Ibuprofen binds noncovalently to a COX enzyme and thus competes with the enzyme's natural substrate. (This is referred to as reversible

covalent bond: bond formed between two atoms that mutually share a pair of electrons

inhibition.) On the other hand, aspirin forms a **covalent bond** to a serine residue in the enzyme, and this bond cannot be broken. (This is called irreversible inhibition.) Acetaminophen does not interact with either COX-1 or COX-2, but it is now understood that it may interact with a newly identified cyclooxygenase, COX-3. Selective targeting of the COX enzymes is an exciting area of pharmacology, in which the challenge continues to be the development of drugs that interact with specific COX enzymes. SEE ALSO ACETYLSALICYLIC ACID; ACETAMINOPHEN; PHARMACEUTICAL CHEMISTRY.

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49
In
INDIUM
114.818

Indium

MELTING POINT: **156.6°C**
BOILING POINT: **2,080°C**
DENSITY: **7.31g/cm^3**
MOST COMMON IONS: **In^{3+}, In^{+}**

metal: element or other substance the solid phase of which is characterized by high thermal and electrical conductivities

Indium is a soft, silver-white **metal**. It was first isolated in 1863 by German chemists Ferdinand Reich and Hieronymus Theodor Richter. Indium was so named because of an intense blue (indigo) line in its emission spectrum. The element is widely distributed in several ores (often in conjunction with zinc) but in low concentrations, accounting for only 0.05 part per million (ppm) of Earth's crust.

oxidation: process that involves the loss of electrons (or the addition of an oxygen atom)

The chemical properties of indium are typical of those of Group 13 of the Periodic Table. Most of indium's oxides, salts, and compounds involve the +3 **oxidation** state (e.g., In_2O_3, $In[NO_3]_3$, and $InCl_3$); many of these compounds are electron-pair acceptors, forming addition compounds with donor molecules (e.g., $InBr_3 \cdot py$, py = pyridine). Neutral, cationic, and anionic complexes are also known. Several interesting compounds are derived from the +1 and +2 oxidation states of the element.

alloy: mixture of two or more elements, at least one of which is a metal

isotope: form of an atom that differs by the number of neutrons in the nucleus

Indium was long regarded as rare and uninteresting, but it has found many interesting applications. Its softness results in its use (alone or in **alloys**) as a bearing metal, as a sealant, and in high-temperature solders. The positron-emitting radioactive **isotopes** ^{111}In and ^{113m}In are used in medical diagnostic imaging.

Organoindium substances are important, especially for the production of materials by metal-organic chemical vapor-phase deposition (MOCVD). This technique involves the thermal decomposition of mixtures of an organoindium compound and a compound such as phosphine (PH_3), leading to the deposition of ordered layers of InP. The resulting compound can be used in the formation of semiconductors and solid-state optical devices (similar to silicon). SEE ALSO INORGANIC CHEMISTRY.

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Industrial Chemistry, Inorganic

Industrial inorganic chemistry includes subdivisions of the chemical industry that manufacture inorganic products on a large scale such as the heavy inorganics (chlor-alkalis, sulfuric acid, sulfates) and fertilizers (potassium, nitrogen, and phosphorus products) as well as segments of fine chemicals that are used to produce high purity inorganics on a much smaller scale. Among these are **reagents** and raw materials used in high-tech industries, pharmaceuticals or electronics, for example, as well as in the preparation of inorganic specialties such as catalysts, pigments, and propellants.

reagent: chemical used to cause a specific chemical reaction

Metals are chemicals in a certain sense. They are manufactured from ores and purified by many of the same processes as those used in the manufacture of inorganics. However, if they are commercialized as **alloys** or in their pure form such as iron, lead, copper, or tungsten, they are considered products of the metallurgical not chemical industry.

metal: element or other substance the solid phase of which is characterized by high thermal and electrical conductivities

alloy: mixture of two or more elements, at least one of which is a metal

The Chemical Industry

The chemical industry adds value to raw materials by transforming them into the chemicals required for the manufacture of consumer products. Since there are usually several different processes that can be used for this purpose, the chemical industry is associated with intense competition for new markets. It is made up of companies of different sizes, including several giants that are engaged in the transformation of some very basic raw materials into final products, as well as medium-size or small companies that concentrate on very few of these steps. The closer to the raw material, the larger the scale of operations; such "heavy" inorganic chemicals are usually manufactured by continuous processes. At the other extreme in terms of scale are the firms that manufacture "specialties," mostly in batch processes, from **"intermediates"** that correspond to chemicals which have already gone through several steps of **synthesis** and purification.

intermediate: a substance that is used to prepare a desired product

synthesis: combination of starting materials to form a desired product

Basic chemicals represent the starting point for the manufacture of inorganic industrial chemicals. They are usually one step away from the raw materials listed in Table 1 and are produced on a very large scale employing continuous processes. The unit price of these products is relatively low, and producing them cheaply and efficiently is a major concern for the companies that manufacture them. Sulfur, nitrogen, phosphorus, and chlor-alkali industries are the main producers of basic inorganic chemicals, and they will often sell them to other industries as well as using them in the manufacture of their own end-products. The basic principles for their production and major uses are indicated here for each of these industries.

Inorganic chemicals produced on an industrial scale can be easily identified. Many of today's large companies started as producers of inorganics,

Inorganic chemicals such as chlorine, produced at this plant in Louisiana, are used in the manufacturing of several chlorides, including PVC and hydrochloric acid.

but as coal—and especially petroleum—became important sources of raw materials, they were integrated into the product chain.

Sources of Inorganic Raw Materials

There are many different sources of raw materials for the manufacture of inorganic chemicals (see Table 1). Very few of them are found in their elemental form. Sulfur is a notable exception. It occurs in underground deposits and can be brought to the surface by compressed air after it is melted by superheated steam. However, increasing quantities of sulfur are recovered from petroleum and natural gas (where they occur as impurities).

Air contains molecular nitrogen and oxygen. They may be separated by **liquefaction** and **fractional distillation** along with **inert** gases, especially argon. Salt or **brine** can be used as sources of chlorine and sometimes bromine, sodium hydroxide, and sodium carbonate, whereas metals such as iron, aluminum, copper, or titanium as well as phosphors, potassium, calcium, and fluorine are obtained from mineral ores. **Saltpeter** was once an important source of nitrogen compounds, but today most ammonia and nitrates are produced synthetically from nitrogen gas in the air.

Recovery and recycling provide increasing amounts of some metals. As environmental concerns increase, these operations will probably become an important source of materials used in the manufacture of certain inorganic chemicals.

liquefaction: process of changing to a liquid form

fractional distillation: separation of liquid mixtures by collecting separately the distillates at certain temperatures

inert: incapable of reacting with another substance

brine: water containing a large concentration of salts, especially sodium chloride (NaCl)

saltpeter: potassium nitrate; chile saltpeter is sodium nitrate

U.S. PRODUCTION OF MINERALS IN 2001

Source	Thousands of Tons	Examples of Uses
Phosphate rock	37,706	Fertilizers, detergents
Salt	49,723	Chlorine, alkali production
Limestone	20,617	Soda ash, lime
Sulfur	10,144	Sulfuric acid production
Potassium compounds	1,323	Caustic potash, fertilizers
Sodium carbonate	11,356	Caustic soda, cleaning formulations

Table 1. U.S. production of minerals in 2001.

The Beginnings of the Chemical Industry

The origins of the chemical industry can be traced to the **Industrial Revolution**. Sulfuric acid and sodium carbonate were among the first industrial chemicals. "Oil of **vitriol**" (as the former was known) played an important role in the manipulation of metals, but its production on an industrial scale required the development of materials that would resist attack. Sodium carbonate was obtained in its anhydrous form, "soda ash," from vegetable material until the quantities produced could no longer meet the rapidly expanding needs of manufacturers of glass, soap, and textiles. This led the Royal Academy of Sciences of Paris, in 1775, to establish a contest for the discovery of a process based on an abundant raw material, sodium chloride, and to Nicolas Leblanc's method for the preparation of soda by converting salt into sulfate

$$2\ NaCl + H_2SO_4 \rightarrow Na_2SO_4 + 2\ HCl$$

followed by conversion of the sulfate to soda with charcoal and chalk

$$Na_2SO_4 + 2\ C + CaCO_3 \rightarrow Na_2CO_3 + CaS + 2\ CO_2$$

Although he did not win the prize, Leblanc's process is associated with the birth of industrial chemistry.

Industrial Revolution: widespread replacement of hand tools by power-driven machines, beginning about 1750 (especially in England)

vitriol: an old term for sulfate of a metal; there are blue (Cu), white (Zn), green (Fe), and rose (Co) vitriols

The industrial production of chemicals was usually based on running reactions that were known to yield the desired products on much larger scales. Success in these endeavors lay much more in the experience and skill of their practitioners than the application of solid chemical principles. This led to serious problems of control and the generation of noxious by-products. The introduction of the Leblanc process in the northwest of England led to a general public outcry against the dark and corrosive smoke that covered the surrounding countryside. The Alkali Act, passed in response in 1863, represents the first legislation that established emission standards.

Sulfuric acid was an essential chemical for dyers, bleachers, and alkali manufacturers. Its production on a large scale required the development of lead-lined chambers that could resist the vapors which were formed when sulfur was burned with nitrates

$$SO_2 + NO_2 + H_2O \rightarrow H_2SO_4 + NO$$

$$NO + 1/2\ O_2 \rightarrow NO_2$$

This process was wasteful and emitted **corrosive gases**. It improved only in the mid-nineteenth century when towers to recycle the gases were finally introduced. The transportation of sulfuric acid was dangerous, and

corrosive gas: gas that causes chemical deterioration alkali manufacturers tended to produce their own as a result. This marked the beginning of the diversification and vertical integration that are characteristic of the chemical industry.

Sulfuric acid was also used in the manufacture of superphosphates, which were produced as fertilizers on a large scale by the mid-nineteenth century. By that time, a solution was found for the complex engineering problems that had hampered the use of the alternative process to produce soda

$$NH_3 + H_2O + CO_2 \rightarrow NH_4HCO_3$$
$$NaCl + NH_4HCO_3 \rightarrow NaHCO_3 + NH_4Cl$$
$$2\ NaHCO_3 \rightarrow Na_2CO_3 + H_2O + CO_2$$

Ernest Solvay, a Belgian chemist, designed a tower in which carbon dioxide reacted efficiently with solid salts. The Solvay process had enormous advantages over the Leblanc process: It did not generate as much waste and pollution; its raw materials, brine and ammonia, were readily available (the latter from gasworks); less fuel was used, and no sulfur or nitrate was involved. In spite of its higher capital costs, it was rapidly adopted and soon became the major source of alkali.

catalytic conversion: catalytic oxidation of carbon monoxide and hydrocarbons in automotive exhaust gas to carbon dioxide and water

Another major process used in the manufacture of inorganic chemicals is the **catalytic conversion** of nitrogen and hydrogen to ammonia. The German chemist Fritz Haber first synthesized ammonia from nitrogen and hydrogen in 1909. Four years later, together with another German, Carl Bosch, he modified the process for the commercial production of ammonia. The Haber (or Haber–Bosch) process represented a technological breakthrough since it required a very specialized plant to handle gases at high pressures and temperatures.

Sulfuric Acid and Sulfates

Sulfuric acid has long been the chemical that is manufactured in the largest quantities on a world scale (see Table 2). Its production is often linked to a country's stage of development, owing to the large number of transformation processes in which it is used.

Sulfuric acid is manufactured from elemental sulfur. Mining was the main source for this element, which was obtained from sulfide-containing ores, or in very pure form from underground deposits by the Frasch process (injection of superheated steam and air into drillings and the separation of the mixture that rises to the surface). The large-scale consumption of petroleum and natural gas has changed this scenario since sulfur occurs as an impurity in most fossil fuels and must be removed before the fuels are processed. These fuels are presently the main source of sulfur, and their relative importance tends to increase with more rigorous controls on emissions.

U.S. PRODUCTION OF INORGANIC CHEMICALS IN 2001

Chemical	Thousands of Tons
Sulfuric acid	40,054
Ammonia	13,046
Sodium chloride	12,019
Phosphoric acid	11,605
Sodium hydroxide	10,687
Nitric acid	7,823
Ammonium sulfate	2,556
Titanium dioxide	1,463
Aluminum sulfate	1,165

Table 2. U.S. production of inorganic chemicals in 2001.

Sulfuric acid is manufactured in three stages

$$S + O_2 \xrightarrow{air} SO_2 + \text{heat}$$
$$2\ SO_2 + O_2 \rightarrow 2SO_3$$
$$SO_3 + H_2O \rightarrow H_2SO_4$$

Since the reaction of sulfur with dry air is exothermic, the sulfur dioxide must be cooled to remove excess heat and avoid reversal of the reaction.

Most plants use reactors with various stages in order to cool the stream for the catalytic step. Conversion by a vanadium pentoxide **catalyst** deposited on a silicate support is the critical step in the process, in which the gaseous stream is passed over successive layers of catalyst. The gas mixture is then passed through an absorption tower. Oleum, the product, is a concentrated solution of sulfuric acid containing excess sulfur trioxide.

catalyst: substance that aids in a reaction while retaining its own chemical identity

As an inexpensive source of acid, a large amount of the sulfuric acid that is produced is used for the manufacture of other mineral acids. It is also used to produce sulfates, such as ammonium sulfate (a low-grade fertilizer), sodium sulfate (used in the production of paper), and aluminum sulfate (used in water treatment), as well as organic sulfates (used as **surfactants**). Sulfuric acid is also a good catalyst for many reactions, including the transformation of ethanol into ethylene or ethyl ether.

surfactants: surface-active agents that lower the surface tension of water; e.g., detergents, wetting agents

Nitrogen Compounds

In general, chemicals containing nitrogen are manufactured from ammonia produced by the Haber process

$$N_2 + 3H_2 \xrightarrow{Fe} 2NH_3$$

Since molecular nitrogen is inert, its reaction with hydrogen requires very severe conditions and a catalyst. An iron catalyst is used. High pressure favors the formation of products, but an increase in temperature will shift the **equilibrium** in the opposite direction. Plants will thus operate under conditions that represent the most favorable balance between operating costs and capital investment.

equilibrium: condition in which two opposite reactions are occurring at the same speed, so that concentrations of products and reactants do not change

Energy consumption is very high, and its cost is an important component along with the starting materials. Nitrogen is easily obtained from air, and hydrogen and can be produced by the shift reaction

$$CO + H_2O \rightarrow CO_2 + H_2$$

or from hydrocarbon reforming

$$CH_4 + 2H_2O \rightarrow CO_2 + 4H_2$$

Further stages are required to assure conversion and to remove carbon dioxide or carbon monoxide from the gas mixture. A mixture of ammonia and synthesis gas ($CO + H_2$) results from the reaction with nitrogen so the two must be separated and the synthesis gas recycled.

Most of the ammonia that is produced is employed as fertilizer or used to manufacture other fertilizers, such as urea, ammonium sulfate, ammonium nitrate, or diammonium hydrogen phosphate. Ammonia is also used in the Solvay process, and it is a starting material for the manufacture of cyanides and nitriles (which are used to make polymers such as nylon and acrylics) as well as aromatic compounds containing nitrogen, such as pyridine and aniline.

The other source of nitrogen compounds in the chemical industry is nitric acid, obtained from the **oxidation** of ammonia

oxidation: process that involves the loss of electrons (or the addition of an oxygen atom)

$$4\ NH_3 + 5\ O_2 \rightarrow 4\ NO + 6\ H_2O$$

$$3\ NO + 3/2\ O_2 \rightarrow 3\ NO_2$$

$$3\ NO_2 + H_2O \rightarrow 2\ HNO_3 + NO$$

The first reaction is run over platinum-rhodium catalysts at around 900°C (1,652°F). In the second and third stages, a mixture of nitric oxide and air circulates through condensers, where it is partially oxidized. The nitrogen dioxide is absorbed in a tower, and nitric acid sinks to the bottom. Nitric acid is mainly used to make ammonium nitrate, most of it for fertilizer although it also goes into the production of explosives. Nitration is used to manufacture explosives such as nitroglycerine and trinitrotoluene (TNT) as well as many important chemical intermediates used in the pharmaceutical and dyestuff industries.

Phosphorus Compounds

The world's major source of phosphorus is apatite, a class of phosphate minerals. Commercially, the most important is fluoroapatite, a calcium phosphate that contains fluorine. This fluorine must be removed for the manufacture of phosphoric acid, but it also can be used to produce hydrofluoric acid and fluorinated compounds.

Phosphoric acid is the starting material for most of the phosphates that are produced industrially. It is obtained from the reaction of the apatite mineral with sulfuric acid

$$\underset{\textit{apatite}}{Ca_{10}F_2\ (PO_4)_6} + 7H_2SO_4 \rightarrow 3Ca(H_2PO_4)_2 + 7\ CaSO_4 + 2HF$$

Silica is present in the mineral as an impurity, and it reacts with hydrofluoric acid to yield silicon tetrafluoride, which can be converted to fluorosilicic acid, an important source of fluorine. More than half of the phosphoric acid that is produced by the reaction of phosphates with sulfuric acid is converted directly to sodium or ammonium phosphates to be used as fertilizer; thus, purity is not a concern.

For products that require high purity, such as detergents and foodstuffs, phosphoric acid is produced from elemental phosphorus (at about four times the cost). An electric furnace operating at 1,400–1,500°C (2,552–2,732°F) is used to form a molten mass of apatite and silica that reacts with coke and reduces the phosphate mineral

$$2\ Ca_3\ (PO_4)_2 + 6\ SiO_2 + 10\ C \rightarrow P_4 + 6\ CaSiO_3 + 10\ CO$$

Concentrating phosphoric acid leads to polyphosphoric acid, a mixture of several polymeric species, a good catalyst and dehydrating agent. Polyphosphate salts are used as water softeners in detergents or as buffers in food. Small quantities of elemental phosphorus are used to make matches, and phosphorus halides to prepare specialty chemicals for the pharmaceutical and agrochemical industries.

Chlor-Alkali Compounds

Industries producing chlorine, sodium hydroxide (also known as caustic soda), sodium carbonate (or soda ash) and its derivatives and compounds based on calcium oxide (or lime) are usually included under this category. As both sodium hydroxide and chlorine have a common raw material, sodium chloride, they are produced in quantities that reflect their equal molar ratio, irrespective of the market for either product. Since they are produced by electrolysis, they require a cheap source of brine and electricity

$$2\ NaCl + 2\ H_2O \rightarrow 2\ NaOH + Cl_2 + H_2$$

Most processes are based on the electrolysis of a sodium chloride solution, but some plants operate with the molten salt. Three different cell types are used in electrolysis in water: mercury cells, diaphragm cells, and membrane cells. Membrane cells are replacing the other two types in modern units, but it may not be economically feasible to convert older plants.

Sodium hydroxide and sodium carbonate are alternative sources of alkali, and their use has followed the availability of raw materials as well as the efficiency of processes developed for their production. Both require sodium chloride and energy and, if limestone deposits are also available, sodium carbonate may be produced by the Solvay process. Limestone consists mainly of calcium carbonate and can be used to produce calcium oxide (or quicklime) and calcium hydroxide (or slaked lime); the oxide may be obtained by heating (1,200–1,500°C, or 2,192–2,732°F) limestone, while the hydroxide, which is more convenient to handle, is obtained by adding water to the oxide

$$CaCO_3 \xrightarrow{heat} CaO + CO_2$$

$$CaO + H_2O \rightarrow Ca(OH)_2$$

Its principal use is in steelmaking, but it also goes into the manufacture of chemicals, water treatment, and pollution control. In the Solvay process, calcium carbonate and sodium chloride are used to produce calcium chloride and sodium carbonate with ammonia (which is recycled) as a medium for dissolving and carbonating the sodium chloride and calcium hydroxide for precipitating calcium chloride from the solution.

As sodium carbonate may be mined directly, its use may be preferred over a manufactured product. It is used mainly in the glass industry. Sodium silicates may be derived from sodium carbonate and in their finely divided form, silica gel, may be used in detergents and soaps.

Sodium hydroxide has many different uses in the chemical industry. Considerable amounts are used in the manufacture of paper and to make sodium hypochlorite for use in disinfectants and bleaches. Chlorine is also used to produce vinyl chloride, the starting material for the manufacture of polyvinyl chloride (PVC), and in water purification. Hydrochloric acid may be prepared by the direct reaction of chlorine and hydrogen gas or by the reaction of sodium chloride and sulfuric acid. It is used as a chlorinating agent for metals and organic compounds.

In certain regions of the world, there are salt deposits or brines that have been enriched by bromine. Commercially, bromine may be extracted by treating the brines with chlorine and removing it by steam.

$$2\ Br^- + Cl_2 \rightarrow Br_2 + 2Cl^-$$

Bromine is used in water disinfection; bleaching fibers and silk; and in the manufacture of medicinal bromine compounds and dyestuffs.

Titanium Dioxide

Titanium dioxide is by far the most important titanium compound. It can be purified by dissolving in sulfuric acid and precipitating the impurities. The solution is then hydrolyzed, washed, and **calcinated**. Alternatively,

calcine: to heat or roast to produce an oxide (e.g., CaO from calcite)

rutile: common name of TiO_2; also a common structural type for compounds with the general composition AB_2

tetrachloride: term that implies a molecule has four chlorine atoms present

ground **rutile** is chlorinated in the presence of carbon and the resulting titanium **tetrachloride** is burned in oxygen to produce the chloride.

Titanium dioxide is found in nature in three crystal forms: anastase, brookite, and rutile. Its extreme whiteness and brightness and its high index of refraction are responsible for its widespread use as a white pigment in paints, lacquers, paper, floor covering, plastics, rubbers, textiles, ceramics, and cosmetics. SEE ALSO Aluminum; Catalysis and Catalysts; Copper; Fertilizer; Haber, Fritz; Iron; Steel.

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Industrial Chemistry, Organic

Industrial organic chemicals are those 100 or so organic compounds produced in the United States in quantities ranging from millions of pounds to billions of pounds per year. Most of them are derived from petroleum (oil) or natural gas. From organic compounds present in petroleum and natural gas are obtained an amazing variety of products that includes many kinds of plastics, synthetic fibers, elastomers, drugs, surface coatings, solvents, detergents, insecticides, herbicides, explosives, gasoline additives, and countless specialty chemicals.

Historically, most organic chemicals had been obtained as by-products from the coking of coal, e.g., from coal oil. During the twentieth century, however, oil and natural gas became the dominant sources of the world's industrial organic chemicals. By 1950 at least half of U.S. industrial "organics" were being made from oil and gas, and by 2000 more than 90 percent of the organic chemical industry was based on petroleum. In fact, the term "petrochemicals" has almost become synonymous with industrial organic chemistry. Yet, less than 10 percent of the oil and gas we consume each year goes into making organic chemicals and the many billions of pounds of products derived from them. Oil and gas are mainly burned as fuel.

Most industrial organic chemistry falls into one of the following categories:

C-1 chemistry, based on synthesis gas (syn gas)

C-2 chemistry, based on ethylene (ethene)

C-3 chemistry, based on propylene (propene)

C-4 chemistry, based on butanes and butenes

BTX chemistry, based on benzene, toluene, and xylenes

Most organic compounds such as those manufactured at this petrochemical plant, are derived from petroleum.

Synthesis gas or "syn gas" is a variable mixture of CO and H_2 produced by the high temperature reaction of water with coal, oil, or natural gas (mainly natural gas in the United States).

$$CH_4 + H_2O \xrightarrow{\Delta} CO + 3H_2 \tag{1}$$

Alkenes or olefins (ethylene, propylene, butenes, and butadiene) are mainly produced via thermal steam cracking. Here, a petroleum fraction is mixed with water and heated briefly (for about 1 second) at 800 to 900°C (1,472–1,652°F), which breaks C–C bonds to yield shorter chains and splits out adjacent hydrogen atoms to form double bonds. The distribution of products obtained is given in Table 1.

BTX (benzene, toluene, and xylenes), the simplest aromatics, are largely produced during catalytic reforming (platforming). In this process a naphtha rich in C_5 to C_9 alkanes is reacted at about 450°C (842°F) and 20 to 30 atm, over a Pt/SiO_2 catalyst, to yield reaction products that are about 60 percent aromatic hydrocarbons. Typically, the products might contain 3 percent benzene, 12 percent toluene, 18 percent xylenes, and 27 percent of C_9 alkylbenzenes (which have high octane numbers and are blended into gasoline). Because benzene is much more in demand for industrial purposes than toluene, the methyl group of toluene is ofte n removed by hydrogenation.

THERMAL STEAM CRACKING PRODUCTS (WEIGHT PERCENT)

Feed	$CH_4 + H_2$	Ethylene	Propylene	Butenes	Gasoline
Ethane	15	80	2	3	trace
Propane	27	42	20	6	5
Butane	25	40	16	10	10
Naphtha (C_{5-9})	16	35	15	9	25

Table 1. Thermal steam cracking products (weight percent).

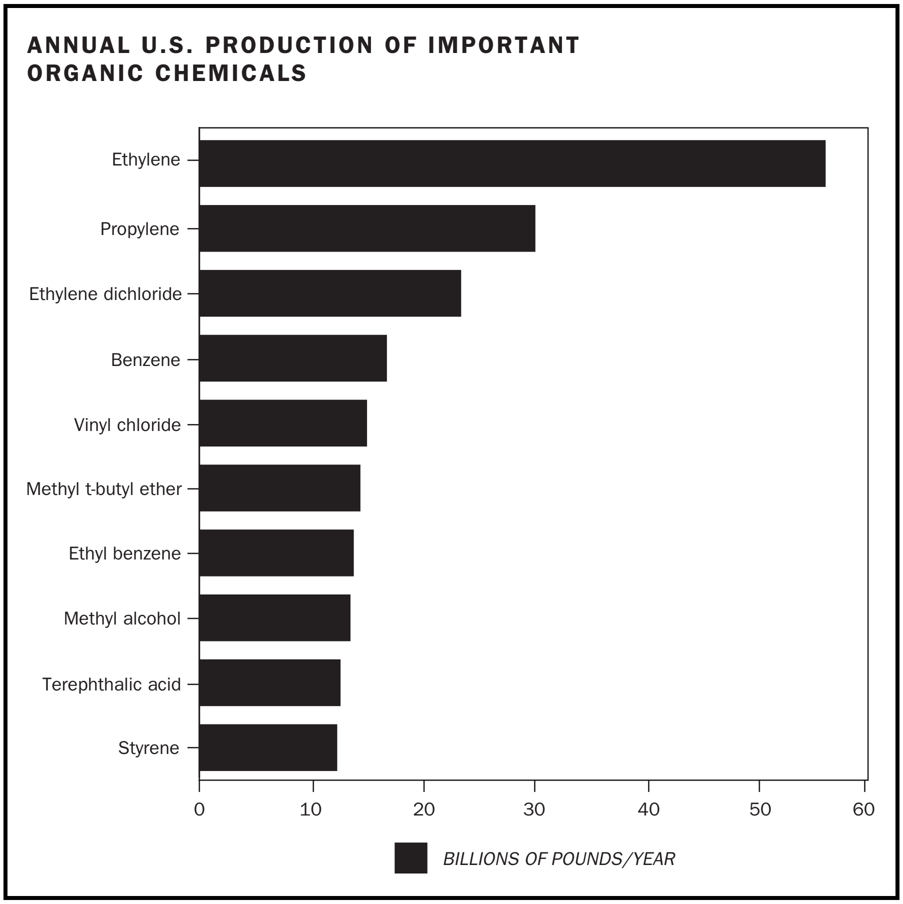
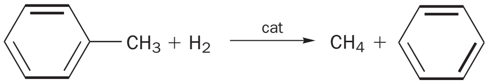


Figure 1. Annual U.S. production of important organic chemicals.



(2)

Production of Some Important Industrial Organic Chemicals

C-1 Chemistry (Syn Gas). Many important organic chemicals can be produced from the CO and H_2 mixture known as syn gas. They range from simple molecules, such as methanol, to high-grade synthetic crude oil.

The basic reaction for conversion of syn gas to mixtures of hydrocarbons is called the Fischer–Tropsch reaction, used in Germany during World War II to produce fuel mixtures for diesel and gasoline engines. Since the 1950s South Africa has also used this reaction, and currently there is much interest in using it to convert natural gas (methane) to more easily transported liquids.

Ammonia (NH_3), although it is not an organic compound, is often considered as part of C-1 chemistry, since it is produced via a reaction that uses hydrogen gas obtained from methane. It is made by the Haber process

$$N_2 + 3\ H_2 \overset{\text{cat}}{\rightleftharpoons} 2\ NH_3 \qquad (3)$$

Ammonia and its derivatives, HNO_3, NH_4NO_3, and $CO(NH_2)_2$, are key fertilizers and ingredients for explosives, and their production consumes nearly 5 percent of the world's natural gas.

Methanol (methyl alcohol, CH_3OH), an important solvent and precursor for many organic chemicals, is made by a process developed in the 1920s

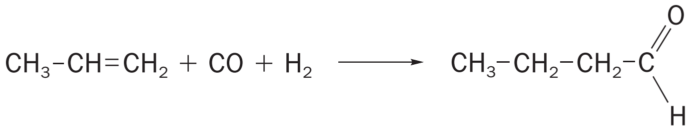
$$CO + 2\ H_2 \rightarrow CH_3OH \tag{4}$$

A major use of methanol is the production of acetic acid via carbonylation.

$$CH_3OH + CO \rightarrow CH_3CO_2H \tag{5}$$

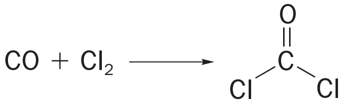
Acetic acid (ethanoic acid, CH_3CO_2H) was for many years made by the simple oxidation of ethanol, but the carbonylation of methanol has now largely displaced this process.

Butanal (butyraldehyde, $CH_3CH_2CH_2CHO$) is made via hydroformylation (the OXO reaction). Although this is a general reaction of syn gas with alkenes to produce aldehydes, the largest poundage reaction of this type (in industry, generating the greatest volume of product) is the reaction of propylene with syn gas to yield butanal.



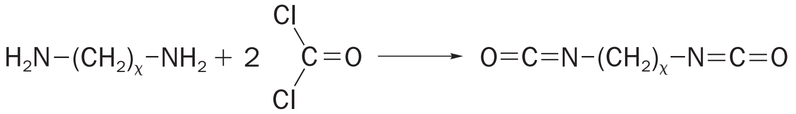
$$CH_3{-}CH{=}CH_2 + CO + H_2 \longrightarrow CH_3{-}CH_2{-}CH_2{-}C({=}O)H \tag{6}$$

Phosgene (Cl_2CO) is made by reacting carbon monoxide from syn gas with chlorine (Cl_2) over activated charcoal at 250°C (482°F).



$$CO + Cl_2 \longrightarrow Cl{-}C({=}O){-}Cl \tag{7}$$

Most phosgene is used in the manufacture of polyurethane plastics via diisocyanates.



$$H_2N{-}(CH_2)_x{-}NH_2 + 2\ Cl_2C{=}O \longrightarrow O{=}C{=}N{-}(CH_2)_x{-}N{=}C{=}O \tag{8}$$

a diamine **phosgene** **a diisocyanate**

C-2 Chemistry (Ethylene or Ethene). With annual worldwide capacity running over 100 million tons, ethylene is the world's largest volume organic compound. Most of it (almost 60%) is used to make polyethylene, the world's highest poundage plastic.

Polyethylene comes in two basic types: high density and low density. The original polymer was a highly flexible branched product, first prepared in 1932 by a process that required high temperatures and ultrahigh pressures. It is now known as low-density polyethylene (LDPE), to differentiate

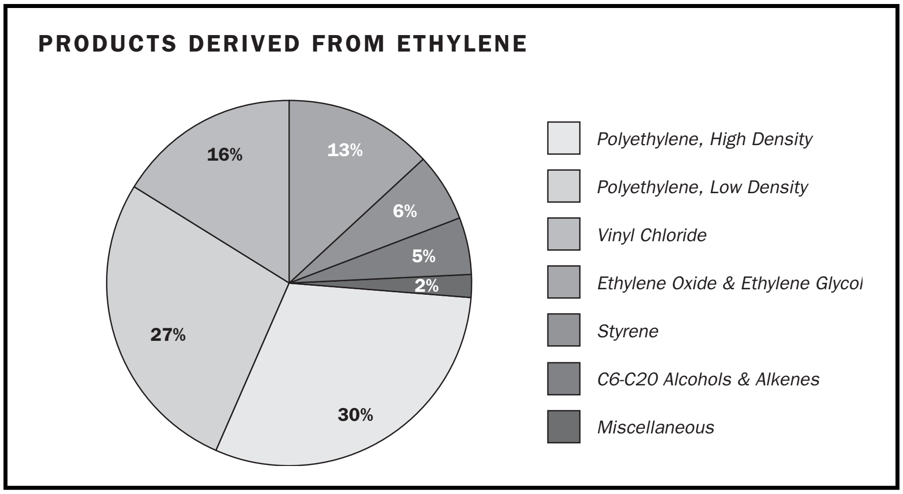
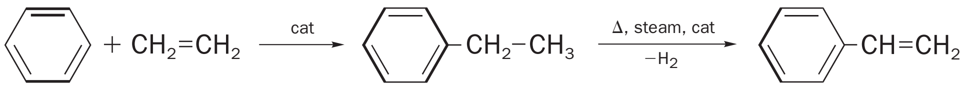


Figure 2. Products derived from ethylene.

it from a linear polymer discovered later and known as high-density polyethylene (HDPE). For many applications the original branched LDPE has now been replaced by linear low-density polyethylene (LLDPE). HDPE is more rigid and less translucent than LDPE or LLDPE, and it has a higher softening point and tensile strength. HDPE is used to make bottles, toys, kitchenware, and so on, whereas LDPE and LLDPE are mainly used for film used in packaging (e.g., plastic bags).

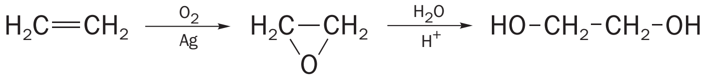
Vinyl chloride ($CH_2{=}CHCl$) is the second-largest-volume chemical made from ethylene. It is made by adding chlorine to ethylene and then thermally cracking out HCl from the intermediate, ethylene dichloride. The vinyl chloride is polymerized to polyvinyl chloride (PVC), also called vinyl, which is used to make pipe, floor covering, wire coating, house siding, imitation leather, and many other products.

$$CH_2{=}CH_2 + Cl_2 \longrightarrow CH_2Cl{-}CH_2Cl \xrightarrow[-HCl]{\Delta} CH_2{=}CHCl \qquad (9)$$


(10)

Styrene (phenylethylene or vinyl benzene, $C_6H_5\text{-}CH{=}CH_2$) is made from ethylene by reaction with benzene to form ethylbenzene, followed by dehydrogenation. Over 50 percent of manufactured styrene is polymerized to polystyrene for toys, cups, containers, and foamed materials used for insulation and packing. The rest is used to make styrene copolymers, such as styrene-butadiene rubber (SBR).

Ethylene oxide is made by air oxidation of ethylene. Most ethylene oxide (about 60%) is converted to ethylene glycol via acid catalyzed hydrolysis.


(11)

$$H_2C{=}CH_2 \xrightarrow[Ag]{O_2} H_2C{-}CH_2\ (\text{bridged by } O) \xrightarrow[H^+]{H_2O} HO{-}CH_2{-}CH_2{-}OH \qquad (11)$$

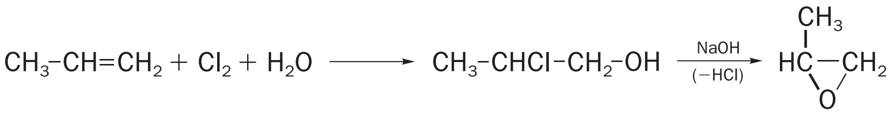
Ethylene glycol ($HOCH_2CH_2OH$) is a toxic dialcohol. Approximately half of what is produced is used as automobile coolant (antifreeze); most of the rest is used to make polyesters for products such as fabrics, rigid films, and bottles.

C-3 Chemistry (Propylene or Propene). Polypropylene manufacture is by far the largest use of propylene. In the late 1950s Karl Ziegler and Giulio Natta developed some special coordination catalysts (aluminum alkyls and titanium salts) that yield very strong addition polymers from propylene. Almost 25 percent of polypropylene is used to make injection-molded articles, such as automotive battery cases, steering wheels, outdoor chairs, toys, and luggage. Another 25 percent is used to make fibers for upholstery, carpets, and special sports clothing. Oligomers (dimers, trimers, and tetramers) of propylene, which are made by acid-catalyzed polymerization, form mixtures known as polygas, used as high-octane motor fuel.

Acrylonitrile ($CH_2{=}CH\text{-}CN$) was made from acetylene and HCN until the 1960s. Today it is made by direct ammoxidation of propylene. Its major use is in making polyacrylonitrile, which is mainly converted to fibers (Orlon). It is also copolymerized with butadiene and styrene to produce high impact plastics.

$$CH_2{=}CH{-}CH_3 + NH_3 + 1/2\ O_2 \xrightarrow{\text{cat}} CH_2{=}CH{-}CN + H_2O \qquad (12)$$

Propylene oxide is made via several methods. The classical one involves treating propylene with chlorine water to produce propylene chlorohydrin, and then using base to split out HCl. The primary use for propylene oxide is its oligomerization (to polypropylene glycols). These products combine with diisocyanates to produce high molecular weight polyurethane foams, which make very good padding for furniture and vehicle seats.



$$CH_3{-}CH{=}CH_2 + Cl_2 + H_2O \longrightarrow CH_3{-}CHCl{-}CH_2{-}OH \xrightarrow[(-HCl)]{\text{NaOH}} \underset{\diagdown\,O\,\diagup}{\overset{CH_3\atop |}{HC}{-}CH_2} \qquad (13)$$

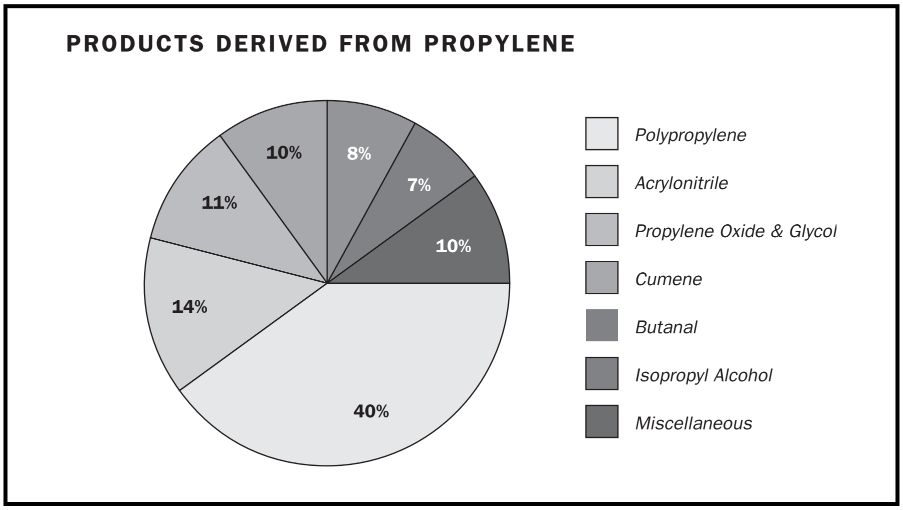
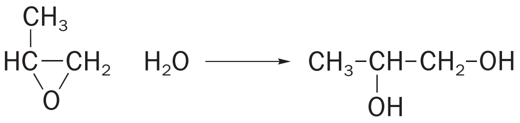


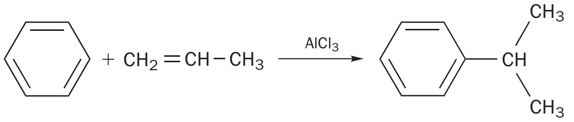
Figure 3. Products derived from propylene.

Manufacture of propylene glycol (CH_3-CHOH-CH_2OH) consumes about 30 percent of the propylene oxide produced. Like ethylene oxide, propylene oxide undergoes hydrolysis to yield the corresponding glycol. Propylene glycol is mainly used to make polyester resins, but it is also used in foods, pharmaceuticals, and cosmetics.

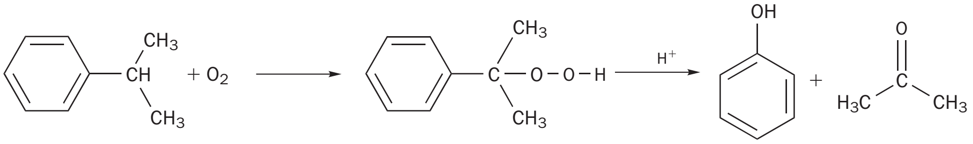


(14)

Cumene (isopropylbenzene) is made by Friedel–Crafts alkylation of benzene with propylene. Although cumene is a high-octane automotive fuel, almost all of the cumene produced is used to make phenol (C_6H_5OH) and acetone [$(CH_3)_2CO$]. Cumene is easily oxidized to the corresponding hydroperoxide, which is readily cleaved in dilute acid, to yield phenol and acetone.



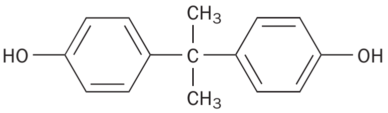
(15)



Cumene **Cumene hydroperoxide** **Phenol** **Acetone**

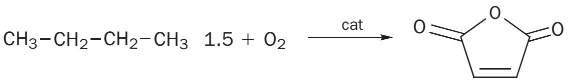
(16)

Phenol and acetone each have a number of important commercial uses, but they also have an important use together. Phenol and acetone can be condensed to form bisphenol A, which is used in the production of polycarbonate and epoxy resins.



(17)

C-4 Chemistry (Butanes, Butylenes, Butadiene). Maleic anhydride is the main chemical made from *n*-butane. A complex catalyst is used for the oxidation reaction. The major uses for maleic anhydride are the making of unsaturated polyester resins (by reaction with glycol and phthalic anhydride) and tetrahydrofuran (by hydrogenation).



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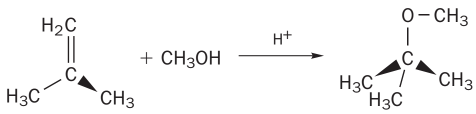


(19)

Methyl-tertiary-butyl ether (MTBE) is one of the leading chemicals currently being made from isobutylene (methyl propene) via the acid-catalyzed addition of methyl alcohol. MTBE has been added to gasoline as a required "oxygenate." However, it is under attack as a groundwater contaminant and is being phased out.

Polyisobutylenes are easily made via the acid-catalyzed polymerization of isobutylene. The low molecular weight polymers are used as additives for gasoline and lubricating oils, whereas higher molecular weight polymers are used as adhesives, sealants, caulks, and protective insulation.

Butyl rubber is made by polymerizing isobutylene with a small quantity of isoprene. Its main uses are in the making of truck tire inner tubes, inner coatings for tubeless tires, and automobile motor mounts.

Hexamethylenediamine [HMDA, H_2H-$(CH_2)_6$-NH_2] is the principal industrial chemical made from butadiene. HMDA is polymerized with adipic acid to make a kind of nylon.

Styrene-butadiene rubber (SBR) accounts for about 40 percent of the total consumption of butadiene. SBR is the material used to make most automobile tires. Other synthetic rubbers, such as polybutadiene and polychloroprene (neoprene), make up another 25 percent of the butadiene market.

ABS resin (acrylonitrile-butadiene-styrene) is a widely used terpolymer that accounts for about 8 percent of the butadiene market.

BTX Chemistry (Benzene, Toluene, Xylene). Styrene, discussed under C-2 chemistry, is one of the main industrial chemicals made from benzene. Most benzene is alkylated with ethylene to form ethylbenzene, which is dehydrogenated to styrene (see Equation 10).

Cumene, discussed under C-3 chemistry, is the second-largest-volume chemical product made from benzene. About 25 percent of manufactured benzene is alkylated with propylene to form cumene. Although its high octane number makes it desirable in gasoline, most cumene is oxidized to the

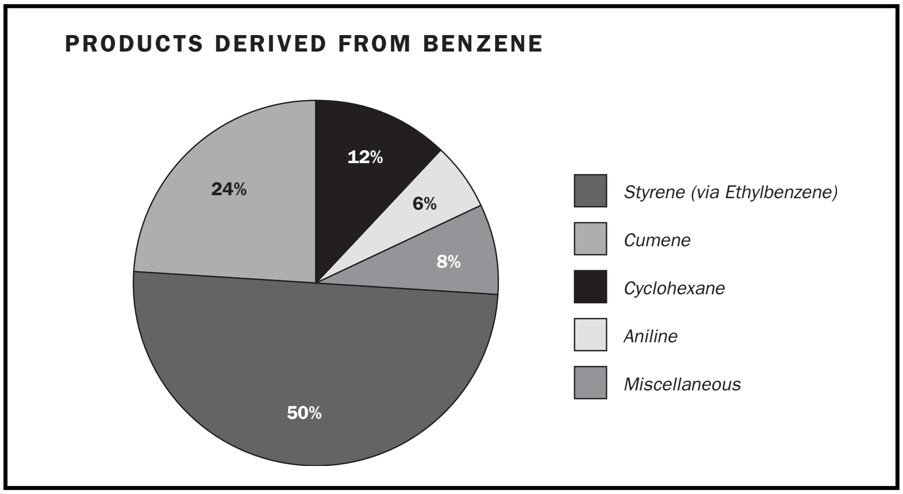
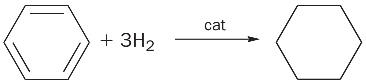


Figure 4. Products derived from benzene.

hydroperoxide, which is readily cleaved to phenol and acetone (see Equation 16).

Cyclohexane (C_6H_{12}) is made by hydrogenation of benzene (over Ni or Pt). Most of it is converted to adipic acid by oxidation, via the intermediaries cyclohexanol and cyclohexanone.

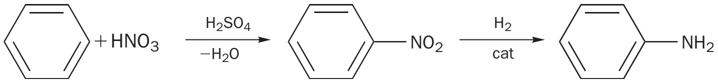


(20)

Adipic acid [$HO_2C(CH_2)_4CO_2H$], the main product of cyclohexane, is reacted with hexamethylene diamine to produce nylon-6,6, a very strong synthetic fiber. Most carpets are made of nylon, as are many silklike garments, some kinds of rope, and many injection-molded articles.

Caprolactam ($C_6H_{11}NO$) is also used to make nylon. Nylon-6 is made by direct polymerization of caprolactam, often obtained by reaction of cyclohexanone with hydroxylamine, followed by rearrangement of the oxime. Although nylon-6,6 is the dominant nylon produced in the United States, nylon-6 is the leading nylon product in Europe.

Aniline ($C_6H_5NH_2$) is made by nitration of benzene to nitrobenzene, followed by hydrogenation over a Cu/SiO_2 catalyst. The major use of aniline is in making diisocyanates, which are used in producing polyurethane materials (e.g., for home insulation).

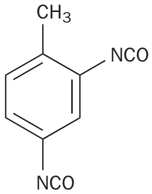


(21)

Alkylbenzene sulfonates ($R\text{-}C_6H_5\text{-}SO_3Na$) are important surfactant compounds used in laundry detergents. Alkylbenzenes (made by the Friedel–Crafts alkylation of benzene using linear olefin molecules that have about twelve carbon atoms) are sulfonated, and the sulfonic acids are then neutralized with NaOH.

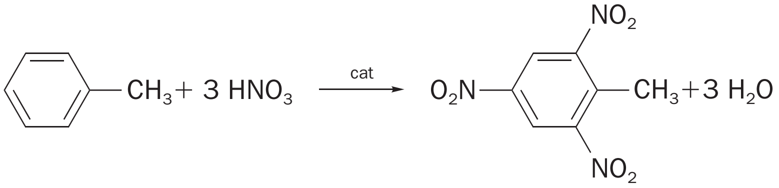
Benzene (C_6H_6), about 40 percent of it, is obtained from toluene by removal of the methyl group (hydrodealkylation, see Equation 2). Benzene production is the primary use of toluene (60%).

Toluene diisocyanate (TDI) is polymerized with diols to produce polyurethanes, which are used to make flexible foam for furniture cushions, mattresses, and carpet pads.



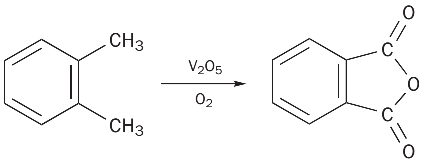
(22)

Trinitrotoluene (TNT) is made via a stepwise nitration of toluene in the 2, 4, and 6 positions. TNT is a high explosive and missile propellant.



(23)

Phthalic anhydride is made by air oxidation of ortho-xylene. About half of phthalic anhydride is used to make plasticizers, especially the compound dioctyl phthalate, for softening polyvinyl chloride plastic. Phthalic anhydride is also used to make unsaturated polyester resins and alkyd paints.



(24)

A Look Toward the Future

Industrial organic chemistry was once based on coal oil. Today it is based mainly on petroleum and natural gas. However, both of these resources are limited in supply and may not last through the twenty-first century.

Because coal reserves are much greater than those of oil and natural gas, perhaps syn gas from coal will become a major source of organic chemicals. However, coal is also a finite raw material, and therefore there is much interest in developing methods for converting renewable resources, such as plants, into industrial organic chemicals. Recently a major chemical company announced its plan to build a small plant for the production of 1,3-propanediol from sugar. This same company has set a goal of producing 25 percent of its feedstocks from renewable resources by 2010. Although this might seem an unrealistic goal, it does indicate current thinking within the chemical industry. SEE ALSO EXPLOSIONS; FERTILIZER; FOSSIL FUELS; ORGANIC CHEMISTRY; PETROLEUM.

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Inert Gases *See Noble Gases.*

Inhibitors

catalysis: reaction induced by a substance that retains its own chemical identity

An inhibitor is any agent that interferes with the activity of an enzyme. Inhibitors may affect the binding of enzyme to substrate, or **catalysis** (via modification of the enzyme's active site), or both. Researchers use enzyme inhibitors to define metabolic pathways and to understand enzyme reaction mechanisms. Many drugs are designed as inhibitors of target enzymes. Inhibition is also a natural phenomenon. Cells regulate metabolic pathways by specific inhibition of key enzymes.

Enzyme inhibitors are divided into two classes, irreversible and reversible. Irreversible inhibition implies destruction or permanent modification of chemical groups in the enzyme. In contrast, reversible inhibitors form a complex with the enzyme that can dissociate and release the active enzyme. An enzyme E can bind either to substrate S, to form an ES complex (which can go on to products) or to inhibitor I, to form the complex EI.

There are two major types of reversible inhibitors, competitive and noncompetitive. Competitive inhibition can be reversed by increasing substrate concentration, whereas noncompetitive inhibition cannot be reversed by adding more substrate.

intermediate: molecule, often short-lived, that occurs while a chemical reaction progresses but is not present when the reaction is complete

The classic example of competitive inhibition is inhibition of succinate dehydrogenase, an enzyme, by the compound malonate. Hans Krebs first elucidated the details of the citric acid cycle by adding malonate to minced pigeon muscle tissue and observing which **intermediates** accumulated after incubation of the mixture with various substrates. The structure of malonate is very similar to that of succinate (see Figure 1). The enzyme will bind malonate but cannot act further on it. That is, the enzyme and inhibitor form a nonproductive complex. We call this competitive inhibition, as succinate and malonate appear to compete for the same site on the enzyme. With competitive inhibition, the percent of inhibition is a function of the ratio between inhibitor and substrate, not the absolute concentration of inhibitor.

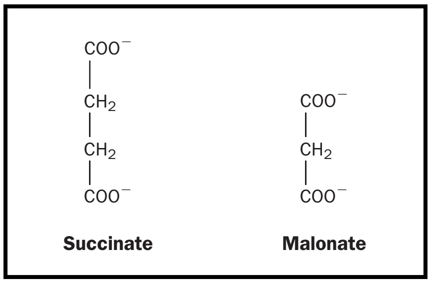
Noncompetitive inhibition is not reversed by adding more substrate. The inhibitor binds at a site on the enzyme other than the substrate binding site. The inhibitor can bind to either free enzyme, forming EI, or to the ES complex, forming EIS. Both EI and EIS are nonproductive.

Irreversible inhibitors are those that permanently disable the enzyme. The complex EI or EIS cannot dissociate, so that these are dead-end complexes. When an irreversible inhibitor is added to the enzyme-containing solution, inhibition may not be complete immediately, but increases gradually with time, as more and more enzyme molecules are modified.

Uses of Inhibitors

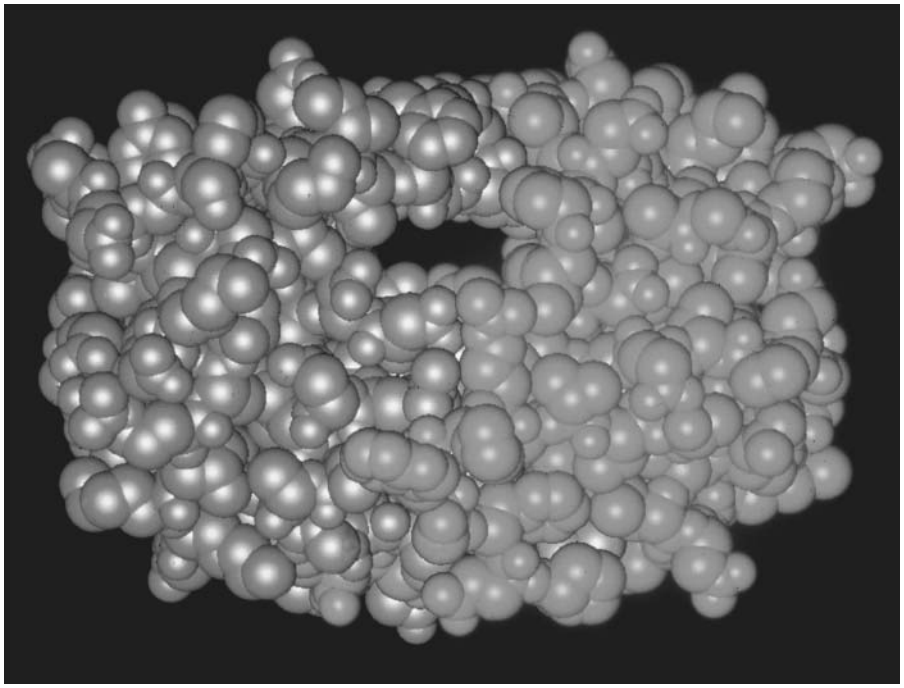
Among the irreversible inhibitors are organophosphorus compounds, which inhibit the enzyme acetylcholinesterase and similar enzymes. Organophosphorous compounds include nerve gases (such as sarin), that work on the human nervous system, and insecticides like malathion.

synthesis: combination of starting materials to form a desired product



Firuge 1. Structures of succinate and malonate.

Many therapeutic drugs are enzyme inhibitors. Important examples are penicillin, which inhibits an enzyme necessary for bacterial cell wall **syn-**



A computer image of the structure of a protease inhibitor.

thesis, and aspirin, an inhibitor of the synthesis of molecules that **mediate** pain and swelling. More recent examples are drugs used in the treatment of human immunodeficiency virus (HIV) and acquired immunodeficiency syndrome (AIDS) that prevent maturation of the virus by inhibiting the HIV protease, and drugs that lower cholesterol by inhibiting a key step in cholesterol **biosynthesis**. SEE ALSO ACTIVE SITE; ENZYMES; KREBS, HANS ADOLF; NEUROCHEMISTRY.

mediate: to act as an intermediary agent

biosynthesis: formation of a chemical substance by a living organism

Adele J. Wolfson

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Inorganic Chemistry

The scope and boundaries of inorganic chemistry were shaped by the earlier field of organic chemistry in the mid-eighteenth and later centuries. Back in these earlier days of chemistry, all chemicals not classified as organic, in other words all chemicals, including minerals and **alloys**, that do not have an origin in living organisms, were placed in a very large category of “inorganic” substances. Many of the first chemists, therefore, used the describable differences between living and nonliving things to help delineate the boundaries of these two areas. Two common distinctions were that, first, organic compounds contained a unique “vital force” that arose from

alloy: mixture of two or more elements, at least one of which is a metal their biological origin and second, as a result, organic compounds could not also be synthesized or reproduced in the laboratory. Of course, both of these distinctions were later disproved, but they clearly helped form the divisions by which chemists have labeled themselves. Today a factor commonly used to distinguish between inorganic and organic substances is the presence of the element carbon. Inorganic chemistry, a vast field of study, is usually defined as the study of any compound that does not contain the element carbon, especially as it occurs in chemically bonded chains and rings that have additional chemical bonds to hydrogen atoms.

It should be noted that as chemists move increasingly toward interdisciplinary work, even this arbitrary distinction cannot adequately describe certain chemical compounds. For example, the solid material Sc_3C_4 (three parts scandium, four parts carbon) has ethane- and propanelike organic fragments (without their hydrogen atoms) that are embedded in a solid matrix of inorganic scandium ions. In another broadly diverse field called organometallic chemistry, chains of organic-like carbon atoms form chemical bonds with inorganic **metal** ions such as zirconium, molybdenum, and nickel. Thus chemistry is becoming increasingly integrated and continuous, with no sharp boundary lines, as chemists realize that closely related ideas, such as chemical bonding and acid/base classifications, can be broadly applied to both complex organic substances as well as to inorganic compounds. In a recent example, an expansion of the concept of aromaticity, normally applied strictly to organic molecules such as benzene (C_6H_6), was found by Lai-Sheng Wang and colleagues to explain also the enhanced stability of inorganic, metal-bonded Al_4^{2-} clusters.

metal: element or other substance the solid phase of which is characterized by high thermal and electrical conductivities

Mono- and Polyatomic Ions

Back in the late 1800s many chemists were hard at work categorizing the known elements according to their bond valences and acid/base characteristics. However, the elements are usually not found free and pure in nature. Instead, they are usually found and worked with in the form of ions and complexes that also contain other elements. When elements combine with each other, ions tend to form, as electrons are transferred to the most **electronegative** elements and partially shared to form chemical bonds. An element that has gained electrons, such as O^{2-}, is called an **anion**, and one that has lost electrons, such as Al^{3+}, is called a cation. In an **aqueous solution**, these ions will interact electrostatically with the solvent, as well as with each other. For example, ions will interact with the partially charged negative and positive regions of H_2O, the most common solvent on Earth. Cations will be surrounded more closely by the oxygen atoms, the more negative region of the H_2O molecules, while an anion will be more closely surrounded by the hydrogen atoms, or the more positive region of the H_2O molecules. The product of this interaction is called a hydrated ion, shown in the following equation, and it is one of the simplest chemical species in solution (e.g., Na^+, K^+, F^-, Cl^-):

electronegative: capable of attracting electrons

anion: negatively charged chemical unit, like Cl^-, CO_3^{2-}, or NO_3^-

aqueous solution: homogenous mixture in which water is the solvent (primary component)

$$M^{n+/-} + H_2O \rightarrow M(H_2O)_x^{n+/-} \ (x \sim 4-6)$$

As the charges of the ions increase across the Periodic Table such as from Na^+ to Sc^{3+} to V^{5+}, or from F^- to O^{2-} to N^{3-}, the bond formed between the ions and the water molecules grows strong enough to weaken and ultimately break the O–H bond. This kind of reaction with water is called hydrolysis. Products of this reaction with cations will yield hydroxides and oxides, such as Sc_2O_3 and V_2O_5, and the solutions will become acidic due to the released hydrogen ions. On the other hand, the reaction with highly charged anions will tend to result in hydrides, NH_3, and the solution will become basic due to the released hydroxide ions. Using this simple picture, which is based on the **electrostatic interaction** of oppositely charged ions, the principle forms of almost all the elements in nature can be qualitatively predicted (see Figure 1).

electrostatic interaction: force that arises between electrically charged particles or regions of particles

"Polyoxocations" and "-anions" are the names given to ions that exist in solution bonded to multiple oxygen atoms, such as ReO_4^{-} and SO_4^{2-}, and occurs only with the highest charged ions, such as Re^{7+} and S^{6+}. These high formal **oxidation** states prevent a large charge buildup on the ion and therefore dramatically lower the basicity of the anion and further association with H^{+}. The sizes of many polyoxoanions may range up to the nanometer scale, with extremely large clusters, more than 100 atoms, existing in molybdenum-containing solutions. Many other types of complex ions exist in different, and less common, solvents. Among the many possible examples are fluorides, TiF_6^{2-} or SiF_6^{2-}; cyanides, $[\mathrm{C\ d(CN)_4}]^{2-}$; chlorides, $PtCl_6^{2-}$; and some organic-bonded ions, $ZrCl_2(Cp)_2$ ($Cp = C_5H_5$; cyclopentadienyl). To understand these compounds, it is first necessary to expand our acid/base definitions.

oxidation: process that involves the loss of electrons (or the addition of an oxygen atom)

Complex Transition-Metal Ions and Compounds

Many reactions and properties that are characteristic of typical acids (H^{+} donors) and bases (OH^{-} donors) occur in chemical compounds that lack any hydrogen or hydroxide ions, such as in nonaqueous solvents. For example, the nitrogen group on a pyridine molecule can donate an electron pair to acidic **metal cations**, such as Zn^{2+} or Cu^{2+}, as well as to H^{+}-containing acids such as HCl. The Zn–N, Cu–N or H–N bond formed neutralizes the acidic character of cations (H^{+} and M^{n+}, discussed above), and thus the pyridine molecule functions much like a base. An expanded definition of bases is necessary to include all chemical species that can donate a pair of electrons. These are commonly called Lewis bases, after Gilbert N. Lewis, who was among the first to note this similarity in solid salts such as $[C_5H_5NH]^{+}Cl^{-}$ or $[Cd(C_5H_5N)_2Cl_2]$. Conversely, any chemical species that can accept a pair of electrons is called a Lewis acid.

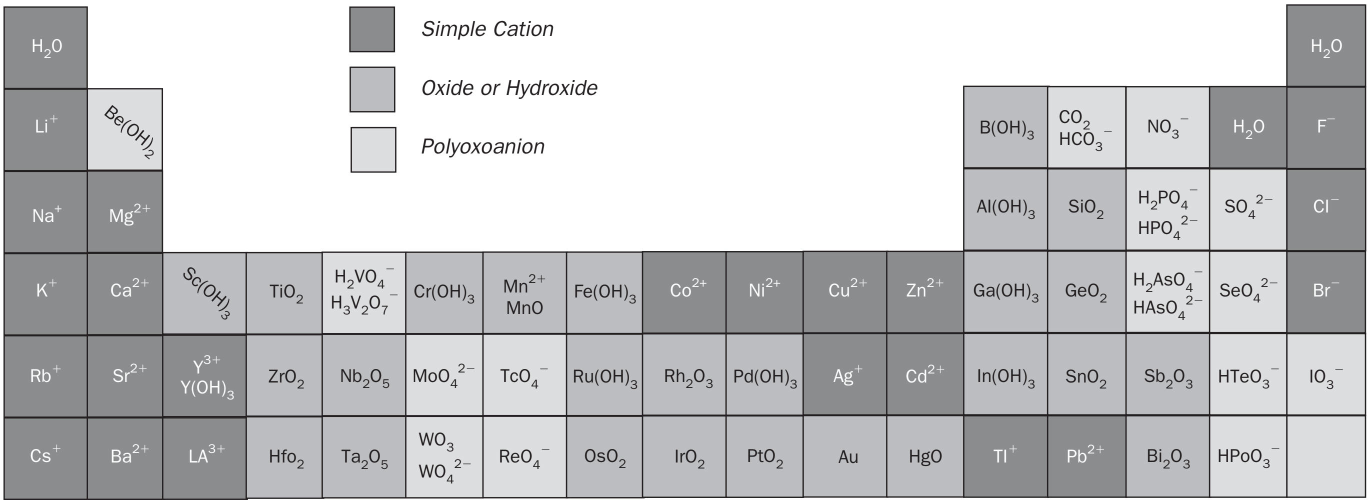
metal cation: positively charged ion resulting from the loss of one or more valence electrons

The bond formed between Lewis acids and bases is termed a **coordinate covalent bond**, and the acid/base pair is called a coordination compound. In coordination compounds, the **ligands** directly bonded to the central metal atom are included within the brackets, as in $[Co(NH_3)_6]^{3+}$, while the nonbonded ions that balance the cation charge, the counter-ions, are located outside the brackets, as in Cl^{-} for $[Co(NH_3)_6]Cl_3$. The subscripts indicate that six ammonia molecules form coordinate **covalent bonds** to Co^{3+}. In other words, the coordination number is six. In the compound $Sn(C_5H_5N)Cl_2$, tin is bonded to one pyridine molecule and to two chloride anions, for a total coordination number of three. The charge on Sn can be calculated by knowing the charges on the ligand species, so that if each pyridine is uncharged and the charge on each Cl is 1–, the net positive charge on Sn must be 2+ to give a neutral molecule. There are hundreds if not

coordinate covalent bond: covalent bond in which both of the shared electrons originate on only one of the bonding atoms

ligand: molecule or ion capable of donating one or more electron pairs to a Lewis acid

covalent bond: bond formed between two atoms that mutually share a pair of electrons



■ Simple Cation

▨ Oxide or Hydroxide

□ Polyoxoanion

H_2O																H_2O
Li^+	$Be(OH)_2$											$B(OH)_3$	CO_2 HCO_3^-	NO_3^-	H_2O	F^-
Na^+	Mg^{2+}											$Al(OH)_3$	SiO_2	$H_2PO_4^-$ HPO_4^{2-}	SO_4^{2-}	Cl^-
K^+	Ca^{2+}	$Sc(OH)_3$	TiO_2	$H_2VO_4^-$ $H_3V_2O_7^-$	$Cr(OH)_3$	Mn^{2+} MnO	$Fe(OH)_3$	Co^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}	$Ga(OH)_3$	GeO_2	$H_2AsO_4^-$ $HAsO_4^{2-}$	SeO_4^{2-}	Br^-
Rb^+	Sr^{2+}	Y^{3+} $Y(OH)_3$	ZrO_2	Nb_2O_5	MoO_4^{2-}	TcO_4^-	$Ru(OH)_3$	Rh_2O_3	$Pd(OH)_3$	Ag^+	Cd^{2+}	$In(OH)_3$	SnO_2	Sb_2O_3	$HTeO_3^-$	IO_3^-
Cs^+	Ba^{2+}	LA^{3+}	Hfo_2	Ta_2O_5	WO_3 WO_4^{2-}	ReO_4^-	OsO_2	IrO_2	PtO_2	Au	HgO	Tl^+	Pb^{2+}	Bi_2O_3	$HPoO_3^-$	

Figure 1. Main form of the ions at a pH = 5.5–7 in a moderately aerated solution. (Redrawn from Wulfsberg, Gary. *Inorganic Chemistry,* p. 127.)

thousands of possible ligands that can attach to the more than forty metal cations, so an almost unlimited number of coordination compounds may be formed. At this point, it is very useful to describe the principles that determine which metal-ligand combinations are preferred.

HSAB Classification

The question of which metal ions prefer to form complex ions with which ligands was answered partly by Ralph G. Pearson during a critical review of hundreds of naturally occurring minerals and synthetic coordination compounds. The general rule of thumb is that hard (Lewis) acids tend to combine with hard (Lewis) bases, and soft acids with soft bases. This is known as the hard-soft acid/base (HSAB) principle. The closer on the Periodic Table that a metal ion is to gold, the softest element, the softer that metal ion is, such as the soft Ag^+ or Cd^{2+} ions. The farther from gold, the harder the metal cation, such as the hard Ca^{2+} ion. For inorganic anions, the hardest is the fluoride anion. The farther away on the Periodic Table, the softer the anion, such as the soft I^- anion. For complex anions, such as PO_4^{3-}, SO_4^{2-}, or CO_3^{2-}, the electron donor groups are the oxygen atoms, and thus these are hard anions.

This concept can explain many of the toxicological effects and the biochemistry of ions and ligands in the body. For example, soft metal cations that are soluble in the digestive tract, such as CH_3Hg^+ and certain Pb salts, are extremely poisonous, as they deactivate key biological enzymes by disrupting their S–H (soft element) bonds. However, many hard metal ions, such as K^+ or Na^+, are essential elements in the body. Examples of toxic soft bases include carbon monoxide, :CO, and the cyanide ion, $:CN^-$, which compete with O_2 for binding to Fe^{2+} in hemoglobin. Representative examples of this concept in major mineral sources include limestone, $CaCO_3$ (hard–hard), fluorite, CaF_2 (hard–hard), sphalerite, ZnS (soft–soft), and argentite, Ag_2S (soft–soft).

Ligand Types

There are further properties of ligands beyond their HSAB characteristics that determine their bonding preferences to metal ions. The simplest ligands, such as pyridine or ammonia, have only a single lone pair of electrons to donate and are called **monodentate** ligands. However, if there are multiple unshared electron pairs, as in pyrazine or thiocyanate, these can be donated to two different metal centers to form a bridge. Alternatively, if these multiple lone pairs are situated at a distance of four to five atoms from each other, the ligand can then "wrap" itself around and donate multiple electron pairs to the same metal cation. These types of ligands are known as chelating ligands, such as in EDTA (ethylenediaminetetraacetate), which has six binding sites. Competition for binding to a metal cation will favor the chelating ligands rather than the monodentate ligands, due to the increased entropy (increased number of particles) of the products:

$$\mathrm{Co(NH_3)_6}^{3+} + \mathrm{EDTA}^{4-} \rightarrow \mathrm{Co(EDTA)}^{1-} + 6\mathrm{NH_3}$$

monodentate: capable of donating one electron pair; literally, one-toothed

In both the reactants and products, cobalt retains a coordination number of six, but the number of individual chemical species increases from two to seven. In another type of ligand, a macrocycle, multiple electron donation sites are held in a rigid conformation for metal binding. This type is best illustrated by many biologically related ligands, such as **chlorophyll**, heme, and **vitamin** B_{12}, which are all tetradentate macrocyclic ligands with nitrogen atom electron donors. These are used in living organisms as moving platforms with photo- and redox-active metal centers, and also as transports for certain ligands such as O_2. Competition for binding to a metal ion between a chelating and macrocyclic ligand will favor the latter, due to entropy gains again, as the more flexible chelating ligand has greater degrees of freedom when unbound. These ligands are highly favorable architectures that transport key ions around the body.

chlorophyll: active molecules in plants undergoing photosynthesis

vitamins: organic molecules needed in small amounts for the normal function of the body; often used as part of an enzyme catalyzed reaction

Additional Areas

There is a great and never-ending story to the many types of complex ions, ligands, compounds, and bonding types that are known and rapidly being discovered by inorganic chemists. Some of these areas include organometallics, metal–metal bonded molecules and solids, multiply bonded main group elements, and intermetallics. SEE ALSO Alkali Metals; Alkaline Earth Metals; Chalcogens; Halogens; Industrial Chemistry, Inorganic; Lewis, Gilbert N.; Semiconductors.

Paul A. Maggard Jr.

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Insecticides

Insecticides are natural or synthetic chemicals used to manage insects pests; they are important for disease control and providing food and fiber for a growing world population. Insect control with chemicals began about 2,000 years ago with the use of natural products, whereas the age of synthetic insecticides began with the introduction of dichlorodiphenyl trichloroethane (DDT) in the 1940s. Here the major classes of insecticides are covered, and important example compounds provided. The discussion is organized topically by mode of action/target tissue. In addition to synthetic materials, natural products are addressed because their use is increasing in "organic farming." This entry then explores the development of plants or viruses genetically engineered to produce insect-selective **toxins**. The harmful effects of insecticides on humans will also be discussed, as well as some nonchemical control techniques.

toxin: poisonous substance produced during bacterial growth

Compounds Affecting Nerves

The pyrethroids are composed of natural pyrethrins, which are isolated from chrysanthemum flowers, as well as newer synthetic materials. Older pyrethroids (e.g., pyrethrins and tetramethrin) **degrade** too rapidly in the environment to be used in agriculture. They are used in buildings, and because of their general safety, they are even applied to humans to control lice. Newer pyrethroids have greater chemical stability (e.g., permethrin and deltamethrin), which allows their use on many types of field crops. Another important use of permethrin is application to mosquito netting. Intoxication by pyrethroids develops rapidly (in 1 to 2 minutes), and involves a rapid loss of normal posture and movement called "knockdown." Pyrethroids affect nerve impulse generation throughout the entire nervous system. Multiple nerve impulses occur when only a single one was expected, and there is an increased release of chemical neurotransmitters as well. These actions result in convulsions, prostration, and death.

degrade: to decompose or reduce to complexity of a chemical

Sabadilla, an extract from the seeds of a tropical lily, is used in home gardens and organic farming operations. It degrades rapidly in the environment, and causes signs of intoxication, and has a mode of action similar to that of pyrethroids. Sabadilla extract has low toxicity to mammals.

The tobacco compound nicotine has been used as an insecticide for over 200 years. It is especially effective against sucking insects, such as aphids, and has excellent **contact activity**. Related compounds are neonicotinoids (e.g., imidacloprid), which have similar insecticidal activity, but are less toxic to mammals. Nicotine and imidacloprid mimic the action of **acetylcholine**, which is the major **excitatory neurotransmitter** in an insect's central nervous system. The action of acetylcholine is stopped by the enzyme acetylcholinesterase, which rapidly breaks down acetylcholine. Nicotine and imidacloprid are also neuroexcitatory, but do so persistently, since they are not affected by acetylcholinesterase. Overstimulation of the nervous system often leads to convulsions, paralysis, and death.

contact activity: process involving the touching of different surfaces

acetylcholine: neurotransmitter with the chemical formula $C_7H_{17}NO_3$; it assists in communication between nerve cells in the brain and central nervous system

excitatory neurotransmitter: molecule that stimulates postsynaptic neurons to transmit impulses

The organophosphorus (OP) and carbamate insecticides are used to control a wide variety of insect pests. The acute toxicity of the OPs and carbamates varies, and many of them have high **mammalian toxicity**. These compounds react chemically with the active site of acetylcholinesterase, producing a blocked enzyme that cannot degrade acetylcholine. The concentration of acetylcholine then builds up and hyperexcitation occurs. The signs of intoxication include restlessness, tremors, convulsions, and paralysis. Blockage of acetylcholinesterase by OPs is persistent, and recovery of the enzyme takes many hours or even days. The mode of action of the carba-

mammalian toxicity: poisonous effect on humans and other mammals

Tent caterpillars on a cocoon, Glacier North Park, Montana. Insecticides are used to eradicate populations of such species where they are not desirable.

mates is similar, except that enzyme blockage is less stable and recovers in a matter of minutes. Among insects, carbamates are particularly toxic to hymenoptera, such as honeybees.

Organochlorines represent one of the oldest groups of synthetic insecticides, with only biodegradable materials such as lindane and endosulfan still used in pest control. High mammalian toxicity was common with organochlorines, but a newer compound, fipronil, has improved selective toxicity toward a variety of insect pests. These insecticides cause hyperexcitability and convulsions by blocking the **inhibitory** neurotransmitter γ-aminobutyric acid (GABA). Normally, GABA has a dampening effect that maintains normal nerve activity. Blocking the effects of GABA removes inhibition, leading to hyperexcitation of the nervous system and convulsions.

inhibitory: relating to the prevention of an action that would normally occur

Deet is an important insect repellant. This compound is applied to skin or clothing, and repels biting flies (e.g., blackflies and mosquitoes). Deet acts on the sensory nerves, causing insects to avoid treated surfaces.

Compounds Affecting Muscles

Ryania consists of the powdered stem of the tropical shrub, *Ryania speciosa*. The extract contains ryanodine and related compounds, and has a low toxicity to mammals. The powder is used as a stomach poison on vegetables and fruit. Ryanodine induces paralysis in insects by direct action on the muscles, resulting in sustained **contraction** and paralysis.

contraction: the shortening and thickening of a functioning muscle or muscle fiber

Avermectins are a group of closely related compounds isolated from the fungus *Streptomyces avermitilis* that are used to control the parasites of humans and animals, as well as arthropod pests in crops. They have fairly high mammalian toxicity, but their movement into treated leaves, oral activity against insect pests, and rapid breakdown in sunlight are all favorable properties. In insects and worms poisoned by avermectin, inactivity and flaccid paralysis occur from its relaxing effect on muscles.

Compounds Disrupting Energy Metabolism

These compounds vary, from the natural product rotenone (from *Derris* or *Lonchocarpus* root, used to control vegetable and fruit insects) to the synthetics sulfluramid and hydramethylnon (used to control mites and cockroaches). Interestingly, the highest acute toxicity to mammals is caused by the natural product rotenone. These compounds affect the production of **adenosine triphosphate (ATP)**, the energy storage molecule of the cell that is produced by mitochondria, the "powerhouse" of the cell. The disruption of energy metabolism and the subsequent loss of ATP result in a slowly developing toxicity, and the effects of all these compounds include inactivity, paralysis, and death.

adenosine triphosphate (ATP): molecule formed by the condensation of adenine, ribose, and triphosphoric acid, HOP(O)OH–O–(O)OH–OP(O)OH–OH; it is a key compound in the mediation of energy in both plants and animals

Insect Growth Regulators

Insects exposed to diflubenzuron and related compounds are unable to form normal cuticle (skin) because their ability to synthesize it is lost. Thus, the cuticle becomes thin and brittle, and is unable to support the insect or to withstand molting, a process requiring the shedding of the old cuticle, as in metamorphosis. Diflubenzuron and other chitin **synthesis** inhibitors have extremely low mammalian toxicity and are used against termites.

synthesis: combination of starting materials to form a desired product

Methoprene and fenoxycarb mimic the action of insect juvenile hormone in molting and reproduction, and have low toxicity to mammals. Exposure at molting produces deformed insects having mixed larval/pupal or larval/adult morphologies, and they disrupt reproductive physiology in adults to effectively serve as a method of birth control.

Tebufenozide acts by mimicking the effects of the insect hormone ecdysone, which along with juvenile hormone, controls the initiation of a molt. Exposure to tebufenozide induces a premature molt that traps the insect in its old cuticle. This compound is especially effective against caterpillars.

Toxins from *Bacillus thuringiensis*

The bacterium *Bacillus thuringiensis* forms an internal crystal that contains a number of insecticidal protein toxins. When eaten by the insect, the crystal dissolves in the midgut, the **toxin** mixture is released, and the proteins are **cleaved** into active forms. The toxins bind specifically to midgut cells and assemble a pore that leads to disintegration of the cells, gut paralysis, and death. *B. thuringiensis* strains have toxins specific for caterpillars, beetles, or flies. They have little or no effect on mammals.

toxin: poisonous substance produced during bacterial growth

cleave: split

Human Toxicity of Insecticides

In mammals DDT and related organochlorines have effects on the endocrine system, including the disruption of thyroid hormone synthesis and mimicking of the effects of **estrogen**. Liver cancer has also been observed in mice exposed to these substances, and there has been one claimed association between exposure to DDT and breast cancer. Epidemiological studies show a consistent connection between exposure to pesticides and the occurrence of Parkinson's disease in rural populations. A well-documented effect of some OPs is organophosphorus-induced delayed **neuropathy**, a slowly developing degeneration of the leg nerves that results in irreversible limping. A spe-

estrogen: female sex hormone

neuropathy: degenerative state of the nerves or nervous system cific hazard of pyrethroids is paresthesia, a tingling or burning sensation in exposed skin.

Ladybugs are natural predators of aphids, mealy bugs, and leaf hoppers and may be introduced into a garden environment as a nonchemical pest-control method.

Nonchemical Control Methods

There is considerable interest in developing genetically enhanced, insect-specific viruses or crop plants that would replace conventional chemical insecticides. Corn, cotton, and potatoes have been engineered to express *B. thuringiensis* toxins to control chewing insects. Although this approach has worked effectively for controlling some pests, others not targeted by the *B. thuringiensis* toxin must be controlled by other means.

Sex pheromones, chemicals that attract one sex of an insect to the other, also have uses in pest control. They are often utilized with traps to monitor the number of pest insects in an area, and when applied in the field at higher levels, they can disrupt reproduction or egg laying.

Biological control involves the introduction of predators and parasitoids to attack pests. The extent of control using this technique varies and can be quite good in some cases, but unforeseen ecological impacts occur when imported species attack nontarget organisms.

Chemical insecticides remain an important tool for managing insect pests of humans, animals, and food and fiber crops. Compounds that are persistent in the environment are no longer used, and the amounts sprayed have dropped from kilograms per acre to grams per acre of active ingredient. Future compounds and technologies will seek to maintain high levels of effectiveness with a reduced impact on the environment and human health. SEE ALSO AGRICULTURAL CHEMISTRY; HERBICIDES; PESTICIDES.

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Insect Repellents *See Insecticides.*

Insulin

Insulin is a small peptide (protein) consisting of fifty-one amino acids synthesized and stored within the pancreas, an organ situated behind the stomach. The protein itself consists of two chains, denoted A and B, linked by disulfide (sulfur-sulfur) bridges between cysteine residues (see Figure 1).

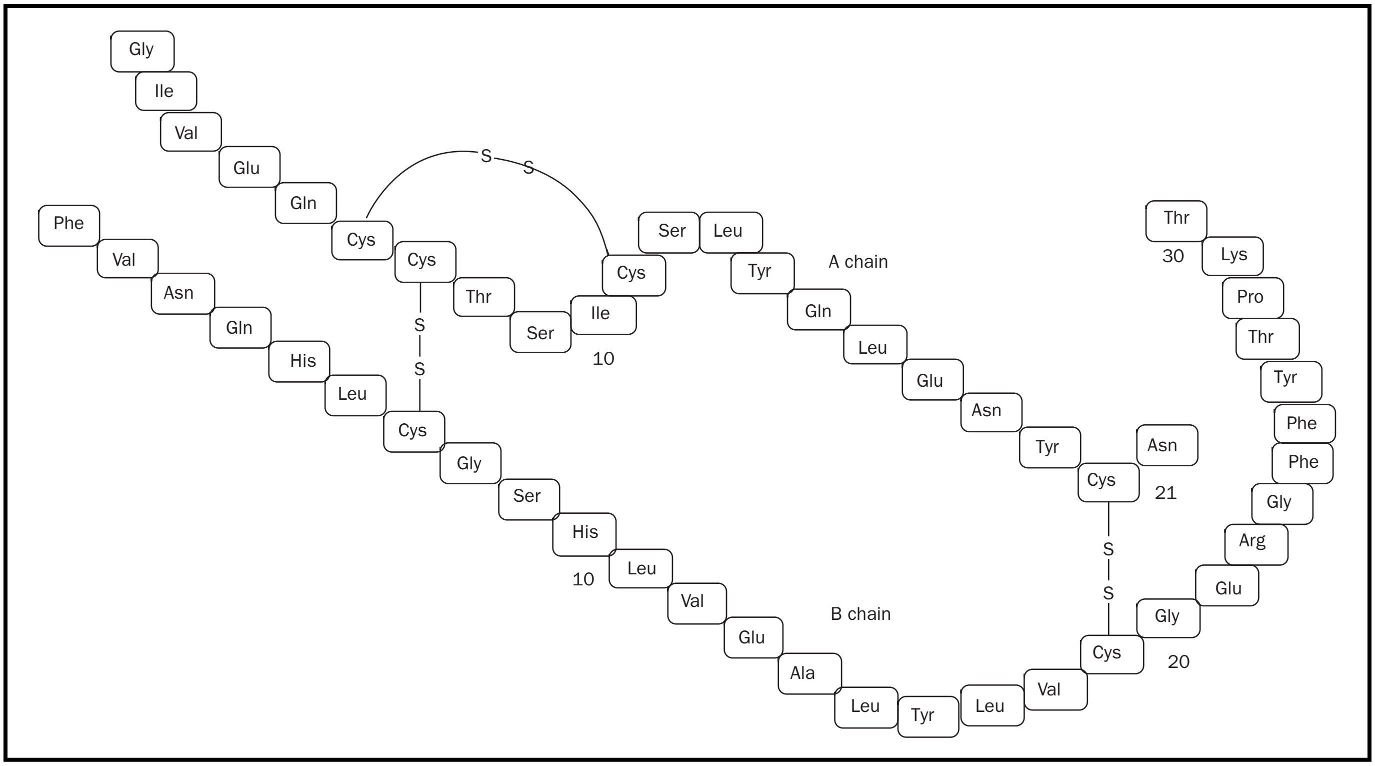

Figure 1. Structure of human insulin.

glucose: common hexose monosaccharide; monomer of starch and cellulose; also called grape sugar, blood sugar, or dextrose

metabolism: the complete range of biochemical processes that take place within living organisms; comprises processes that produce complex substances from simpler components, with a consequent use of energy (anabolism), and those which break down complex food molecules, thus liberating energy (catabolism)

receptor: area on or near a cell wall that accepts another molecule to allow a change in the cell

Insulin is a hormone, a chemical transported in the blood that controls and regulates the activity of certain cells or organs in the body. When blood sugar levels rise following a meal, the pancreas is stimulated to release insulin into the bloodstream. In order for tissues to absorb **glucose** from the blood, they must first bind insulin. Glucose **metabolism** is necessary for cell growth and energy needs associated with cell function. When insulin binds to **receptors** on cell membranes, glucose transporter proteins are released from within the cell to the surface of the cell membrane. Once on the exterior surface of cells, glucose transporters can carry sugar from the blood into the tissue where it is metabolized. Without insulin, cells cannot absorb glucose and effectively starve.

A deficiency in insulin production results in a condition called diabetes mellitus. Approximately 6.2 percent of the population in the United States is affected with diabetes. Type 1 diabetics account for 10 percent of those individuals suffering from diabetes mellitus. It is also known as juvenile diabetes and generally develops in young people, typically between the ages of ten and fifteen years, as a result of an autoimmune disorder. Why the body's immune system turns on itself, attacking and destroying beta cells, the pancreatic cells in which insulin is synthesized, is not clear. The unfortunate consequence is insulin deficiency.

The majority of individuals afflicted with diabetes mellitus suffer from type 2 diabetes. The onset of type 2 diabetes occurs much later than for type 1 and typically in people over the age of fifty. The pancreas of type 2 diabetics continues to produce and release insulin. However, cells do not respond appropriately to insulin levels in the blood. This condition is known as insulin-resistance and is associated with obesity and high blood pressure. Children who are obese can also develop type 2 diabetes.

Gestational diabetes affects 3 to 5 percent of pregnant women. Onset generally occurs in the fifth or sixth month of pregnancy. In pregnant women, the placenta produces hormones to support the growing fetus. Some of these hormones (e.g., **estrogen** and cortisol) interfere with the actions of insulin. Insulin-resistance develops despite adequate blood insulin levels. Gestational diabetes does not last beyond pregnancy and the condition disappears after delivery.

estrogen: female sex hormone

Before the discovery of insulin, type 1 diabetics usually died within a few years of onset of the disease. During the early 1920s, a young Canadian physician, Frederick Grant Banting, working with John James Rickard Macleod, professor of physiology at the University of Toronto, and Charles Best, a medical student, discovered insulin while performing investigations on extracts acquired from dog pancreas. Soon after, Banting and Macleod were awarded the 1923 Nobel Prize in physiology or medicine for their discovery (Banting reportedly split his share of the prize money with Best).

Insulin was rapidly put into clinical use, chiefly through the efforts of August Krogh, a Danish scientist who cofounded the Nordic Insulin Laboratory in Copenhagen, Denmark, for the production of insulin. Large quantities of insulin were initially acquired from the pancreatic tissues of slaughtered animals, typically cows and pigs. Although bovine (cow) and porcine (pig) insulin are still the major components of commercially available insulin in the United States, the use of human insulin preparations is rapidly growing. Since the 1980s, recombinant **DNA** techniques have made human insulin available for clinical use. Genetically modified strains of *Escherichia coli* bacteria or *Saccharomyces cerevisiae* (baker's yeast) containing human genes coding for insulin have been developed for the mass production of human insulin.

DNA: deoxyribonucleic acid—the natural polymer that stores genetic information in the nucleus of a cell

Insulin is not a cure for diabetes. It does, however, allow diabetics, especially those with type 1 diabetes, to gain some control over their condition. Insulin is typically administered by subcutaneous (under the skin) injection. There are four principal types of insulin preparations commercially available. Insulin lispro (ultra-short-acting insulin) is rapidly absorbed into the blood and lasts only 3 to 4 hours. Regular insulin, on the other hand, takes 30 minutes to become effective, and lasts 5 to 7 hours. Lente and NPH (neutral protamine Hagedorn) insulin preparations are longer-acting formulations typically administered every 12 hours. Finally, mixtures of insulin preparations are also commercially available. Typical mixtures consist of 70 percent NPH and 30 percent insulin lispro. SEE ALSO GENETIC ENGINEERING; GLYCOLYSIS.

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Interferon

Interferon, a small protein containing fewer than two hundred amino acids, is an interesting example of a biologically active polypeptide. There are three classes of interferon, labeled by the first three letters of the Greek alphabet. Interferon-α is used to treat leukemia, hepatitis B and C, and Kaposi's sarcoma. Interferon-β finds use as a treatment for multiple sclerosis and interferon-γ has applications in treating a rare genetic disorder called granulomatous disease.

Cells within the body synthesize interferon when experiencing stress from incidents such as viral attack. When interferon is released into the bloodstream by an infected cell, it helps signal an immune response to the invader. Other mechanisms that interferon activates in the fight against viral infections are less understood. It is hypothesized that in addition to signaling the immune system they somehow inhibit the ability of viruses and tumor cells to reproduce. Research to further the understanding of how interferon works is inhibited by the fact that, aside from humans, only a few other animals have cells that make interferon. Many studies of how drug molecules work are carried out first with animals, but for interferon, this type of study is less productive.

Dr. Alick Isaacs and Dr. Jean Lindenmann discovered interferon in 1957 in Great Britain. In an experiment, they mixed live viruses with egg membranes and unexpectedly found that the viruses did not grow. They did not know what caused this observation and simply indicated something interfered with the virus, so the term "interferon" was coined. They eventually identified the polypeptide and were able to isolate it from various cells, including those taken from calves, monkeys, and humans.

Interferon is produced naturally in very small quantities. When it originally was introduced as a form of medical treatment, the expense associated with isolating the compound from sources such as blood made it prohibitively expensive. Interferon became viable as a medical intervention only through the application of genetic engineering. The gene that tells a cell how to construct interferon is introduced into *Escherichia coli* bacteria. These bacteria are grown in culture and they produce the interferon. Because the bacteria can be grown relatively quickly, large quantities of interferon can be generated with this method. While many people tend to react to the phrase "genetic engineering" with some fear, interferon represents an excellent example of how advances in medical treatment were made possible only by its application. SEE ALSO AMINO ACID; PROTEIN.

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International System of Units

The International System of Units (SI), which began as the decimal metric system during the French Revolution, deals with the definitions, terminology, proper usage, and modifications of scientific units. The metric system was established officially in France on June 22, 1799, and consisted of two standard measures: the meter for length and the kilogram for mass. The German mathematician and astronomer Carl Friedrich Gauss (1777–1855) promoted the use of the metric system and in 1832 added the second as the unit of time. The British Association for the Advancement of Science (BAAS) in 1874 introduced an alternative system, known as the CGS system, whose units of measure were the centimeter, gram, and second. Until 1889 the scientific community had two metric standards for length, mass, and time.

The first General Conference on Weights and Measures (Conférence Générale des Poids et Mesures, or CGPM) in 1889 sanctioned a new system, the MKS system, that included the international prototypes for the meter and kilogram and the astronomical second as the unit of time. Fifty years later, in 1939, the International Committee for Weights and Measures (Comité International des Poids et Mesures, or CIPM), under authority of the CGPM, proposed a four-unit MKS system with the addition of the ampere for electric current. Official recognition of the ampere had to wait until 1946, after World War II had ended.

The tenth CGPM in 1954 added two more standards when it officially approved both the kelvin for thermodynamic temperature and the candela for luminous intensity. In 1960 the eleventh CGPM renamed its MKS system of units the International System of Units, and in 1971 the fourteenth CGPM completed the seven-unit system in use today, with the addition of the mole as the unit for the amount of a substance, setting it equal to the gram-molecular weight of a substance.

SI units fall into two groups: basic units and derived units. The basic units are the seven mutually independent units (see Table 1) and include the meter, kilogram, second, ampere, kelvin, mole, and candela. They represent,

SI BASIC UNITS

Base Quantity	Base Unit	Symbol
Length	meter	m
Mass	kilogram	kg
Time	second	s
Electric current	ampere	A
Thermodynamic temperature	kelvin	K
Amount of substance	mole	mol
Luminous intensity	candela	cd

SOURCE: Taylor, Barry N., ed., and National Institute of Standards and Technology (1995). *Guide for the Use of the International System of Units (SI).* Special Publication 811. Washington, DC: U.S. Government Printing Office.

Table 1. SI basic units.

Table 2. SI-derived units.

SI-DERIVED UNITS

Derived Quantity	Name	Symbol
Area	square meter	m^2
Volume	cubic meter	m^3
Velocity	meter per second	m/s
Acceleration	meter per second squared	m/s^2
Wave number	reciprocal meter	m^{-1}
Mass density	kilogram per cubic meter	kg/m^3
Specific volume	cubic meter per kilogram	m^3/kg
Current density	ampere per square meter	A/m^2
Magnetic field strength	ampere per meter	A/m
Amount-of-substance concentration	mole per cubic meter	mol/m^3
Luminance	candela per square meter	cd/m^2
Mass fraction	kilogram per kilogram, which may be represented by the number 1	kg/kg = 1

SOURCE: Taylor, Barry N., ed., and National Institute of Standards and Technology (1995). *Guide for the Use of the International System of Units (SI).* Special Publication 811. Washington, DC: U.S. Government Printing Office.

respectively, length, mass, time, electric current, thermodynamic temperature, amount of substance, and luminous intensity. Derived units, as the name indicates, are units obtained algebraically from the seven basic units (see Table 2).

The CIPM has approved twenty prefixes for SI units (see Table 3) and permits the use of any SI prefix with an SI unit, with one exception. The SI unit for mass, the kilogram, already has a prefix in its name and can have no other SI prefix. To use prefixes with a unit for mass, the rule is to remove the "kilo" prefix and add the new prefix to "gram" (unit symbol g), as in milligram and its abbreviation mg.

The CIPM has developed several rules to ensure the proper use of SI units and to eliminate ambiguity from scientific communications. The National Institute of Standards and Technology in Washington, D.C., makes available a complete detailed list of the rules.

SI units, or those the CIPM recognizes, express quantity values. Other units, if used, may appear in parentheses after the appropriate SI or recognized units. The CIPM uses no abbreviations for names and only accepted unit symbols, unit names, prefix symbols, and prefix names. It makes no differentiation in symbol use for a plural, and the only time a period follows a unit symbol is at the end of a sentence. The addition of subscripts does not change a unit name or symbol.

Mathematical operations have specific rules for the use of mathematical symbols with SI units. A space or a half-high dot represents the multiplication of units; a negative exponent, horizontal line, or slash represents the division of units, and if these mathematical symbols appear in the same line, parentheses must differentiate them. The percent sign (%) denotes the number 0.01 or 1/100, so that 1% = 0.01, 30% = 0.30, and so forth. Arabic numerals with the appropriate SI or recognized unit indicate the values of quantities. Commas are not used to separate numbers into groups of three. If more than four digits appear on either side of the decimal point, a space separates the groups of three.

PREFIXES

Factor	Name	Symbol
10^{24}	yotta	Y
10^{21}	zetta	Z
10^{18}	exa	E
10^{15}	peta	P
10^{12}	tera	T
10^{9}	giga	G
10^{6}	mega	M
10^{3}	kilo	k
10^{2}	hecto	h
10^{1}	deka	da
10^{-1}	deci	d
10^{-2}	centi	c
10^{-3}	milli	m
10^{-6}	micro	μ
10^{-9}	nano	n
10^{-12}	pico	p
10^{-15}	femto	f
10^{-18}	atto	a
10^{-21}	zepto	z
10^{-24}	yocto	y

SOURCE: Taylor, Barry N., ed., and National Institute of Standards and Technology (1995). *Guide for the Use of the International System of Units (SI).* Special Publication 811. Washington, DC: U.S. Government Printing Office.

Table 3. Prefixes.

Table 4. Non-SI units accepted for use.

NON-SI UNITS ACCEPTED FOR USE

Name	Symbol	Value in SI units
Minute (time)	min	1 min = 60 s
Hour	h	1 h = 60 min = 3,600 s
Day	d	1 d = 24 h = 86,400 s
Degree (angle)	°	1° = (PI/180) rad
Minute (angle)	'	1' = (1/60)° = (PI/10,800) rad
Second (angle)	''	1'' = (1/60)' = (PI/648,000) rad
Liter	L	1 L = 1 dm^3 = 10^{-3} m^3
Metric ton	t	1 t = 10^3 kg
Neper	Np	1 Np = 1
Bel	B	1 B = (1/2) ln 10 Np
Electronvolt	eV	1 eV = 1.602 18 x 10^{-9} J, approximately
Unified atomic mass unit	u	1 u = 1.660 54 x 10^{-27} kg, approximately
Astronomical unit	ua	1 ua = 1.495 98 x 10^{11} m, approximately

SOURCE: Taylor, Barry N., ed., and National Institute of Standards and Technology (1995). *Guide for the Use of the International System of Units (SI).* Special Publication 811. Washington, DC: U.S. Government Printing Office

Numbers, unit symbols, and names have set rules for mixing and differentiation for clarity of text and mathematical operations. These include a space between a numerical value and its unit symbol, indicating clearly the number a symbol belongs to in a given mathematical calculation, and no mixing of unit symbols and names nor making calculations on unit names. Different symbols represent values and units and the unit symbol should follow the value symbol separated by a slash. SI requires the use of standardized mathematical symbols and the explicit writing of a quotient quantity.

SI units and their symbols have distinctive type styles. Items given in italic type are variables, quantity symbols, superscripts and subscripts if they represent variables, quantities, or running numbers. Items given in roman type are unit symbols, superscripts, and subscripts that are descriptive. The typeface used in the surrounding text of the document does not change these rules.

Several terms used in vernacular science are not appropriate for scientific communication. The CIPM does not use such terms as parts per million, parts per billion, or parts per trillion or their abbreviations as expressions of quantities. The word “weight” is a force with the SI unit of newton, not a synonym for mass with the SI unit of kilogram. Terms for an object and quantities describing the object require a clear different action. Normality, molarity, and molal are obsolete terms no longer used.

Several important and widely used units are not officially part of the SI, but the CIPM has accepted them for use with SI units (see Table 4). They include the liter, day, hour, minute, electronvolt, and degree. Although the CIPM adopted the liter in 1879, it is not a current SI unit. Its symbol (L in the United States, l everywhere else) causes some confusion, but the CIPM has approved neither.

In the United States, the National Institute of Standards and Technology (NIST) also has compiled a list of units outside the SI that it has approved for domestic use (see Table 5). It recommends defining them in terms of accepted SI units. The CIPM does not encourage the use of units on the NIST list but accepts all of them, excluding the curie, roentgen, rad,

Table 5. Non-SI units approved by the NIST.

NON-SI UNITS APPROVED BY THE NIST

Name	Symbol	Value in SI units
Nautical mile	n/a	1 nautical mile = 1,852 m
Knot	n/a	1 nautical mile per hour = (1,852/3,600) m/s
Are	a	1 a = 1 dam^2 = 10^2 m^2
Hectare	ha	1 ha = 1 hm^2 = 10^4 m^2
Bar	bar	1 bar = 0.1 MPa = 100 kPa = 1,000 hPa = 10^5 Pa
Angstrom	Å . . .	1 Å . . . = 0.1 nm = 10^{-10} m
Barn	b	1 b = 100 fm^2 = 10^{-28} m2
Curie	Ci	1 Ci = 3.7 x 10^{10} Bq
Roentgen	R	1 R = 2.58 x 10^{-4} C/kg
Rad	rad	1 rad = 1 cGy = 10^{-2} Gy
Rem	rem	1 rem = 1 cSv = 10^{-2} Sv

SOURCE: Taylor, Barry N., ed., and National Institute of Standards and Technology (1995). *Guide for the Use of the International System of Units (SI).* Special Publication 811. Washington, DC: U.S. Government Printing Office.

and rem, which American scientists have nonetheless continued to use. SEE ALSO Measurement; Mole Concept.

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Iodine

53
I
IODINE
126.9

MELTING POINT: **113.7°C**
BOILING POINT: **184.3°C**
DENSITY: **4.94 g/cm^3**
MOST COMMON IONS: **IO^-, IO_3^-, IO_6^{5+}**

Iodine is the heaviest of the **halogen** family of elements, excluding the radioactive element astatine. It was discovered in 1811 by French chemist Bernard Courtois, who isolated the element from seaweed. The element is named for its color in the gas **phase** (the Greek word *iodes* means "violet").

halogen: element in the periodic family numbered VIIA (or 17 in the modern nomenclature) that includes fluorine, chlorine, bromine, iodine, and astatine

phase: homogeneous state of matter

At normal temperatures and pressures, iodine is a shiny, purplish-black or gray solid. Near room temperature, iodine sublimes (i.e., it does not melt to form a liquid but goes directly from the solid to the gas phase). It is found at a level of about 60 parts per billion (ppb) by weight in seawater but its concentration is enhanced in marine organisms.

As with the other halogens, iodine is a diatomic molecule. It is always found in nature in a combined state, often as iodide salts where it has a −1 **oxidation** number. Compounds in which iodine is found to have oxidation numbers of 7, 3, 5, and 1 are also well known. Iodine is prepared commercially by treatment of natural salt solutions (seawater or brines) with chlorine (a more reactive halogen), according to the reaction:

oxidation: process that involves the loss of electrons (or the addition of an oxygen atom)

$$2\ I^- + Cl_2 \rightarrow I_2 + 2\ Cl^-$$

Iodine is necessary for the proper function of the thyroid gland in humans. Dietary deficiencies can be avoided by the occasional consumption of seafood or by using iodized salt, which combines common table salt (NaCl) with potassium iodide (KI). Iodine is a useful antiseptic, either as tincture of iodine (an alcohol solution of I_2), or as an **aqueous solution** of providone iodine (Betadine). SEE ALSO HALOGENS; INORGANIC CHEMISTRY.

aqueous solution: homogenous mixture in which water is the solvent (primary component)

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Ion Channels

Ion channels play a fundamental role in the way cells communicate. They generate the electrical signals that make hearts beat and muscles contract, and allow brains to receive and process information. This communication between cells allows for the orchestration of physical and mental activities in humans. Many diseases result from ion channels that do not function properly.

Ion channels are transmembrane proteins that span the cell membrane and are formed from one or more protein subunits. The channels are shaped like tunnels, which form pores through the plasma membrane. The pores have gates that open and close to allow ions to diffuse down their chemical gradient and move in or out of a cell. Ion channels are specific for certain types (and combinations of types) of ions, such as chloride, sodium, potassium, and calcium.

Ions are atoms or molecules that have gained or lost one or more electrons to give them either a net positive or negative electrical charge. They are unequally distributed, creating a separation of charge across a membrane, resulting in an electrical potential. When an ion channel is open, a million ions can flow in or out of the cell per second. This causes an electrical signal or current, which allows cells to communicate very quickly.

There are two major classes of ion channels defined by the way the channel opens: ligand-gated and voltage-gated. Ligand-gated ion channels

receptor: area on or near a cell wall that accepts another molecule to allow a change in the cell

open when a specific chemical signal called a neurotransmitter is released from one cell, diffuses through a gap known as a synapse, and binds to **receptors** on ion channels of a second cell. The binding of the neurotransmitter causes the ion channel gate to open. Voltage-gated ion channels have sensors for the electrical potential across the membrane. They open when the cell is at a specific membrane potential. Some other channels can open due to mechanical stress or the levels of signaling molecules inside the cell.

An important function of ion channels is to regulate when cells are at rest and when they are communicating. When a neuron is at its resting potential, it is not sending a signal to any other cells. The inside of a neuron at rest is more negative than the outside. If a neuron is stimulated to communicate with other cells, ion channels open to make the inside of the cell more positive than the resting potential. The neuron will reach a threshold and fire an action potential, where voltage-gated ions channels open, allowing sodium ions to rush in and potassium ions to rush out of the cell. Action potentials propagate and repeat many times to carry a signal the length of a nerve cell. This cell can then continue to communicate by releasing neurotransmitter to bind ligand-gated ion channels on another cell.

A number of diseases occur when ion channels do not function properly. Some examples are epilepsy, cystic fibrosis, heart arrhythmia, and high blood pressure. Ion channels are also the target of many types of drugs and toxins, which can alter the fundamental communication between cells. SEE ALSO CONCENTRATION GRADIENT; MEMBRANE; NEUROTRANSMITTERS; TRANSMEMBRANE PROTEIN.

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77
Ir
IRIDIUM
192.22

Iridium

MELTING POINT: 2,454°C
BOILING POINT: 3,590°C
DENSITY: 22.6 g/cm^3 (at 25°C)
MOST COMMON IONS: Ir^{3+}

alloy: mixture of two or more elements, at least one of which is a metal

Iridium was discovered by English chemist Smithson Tenant. It was named after the Greek goddess Iris (a goddess related to the rainbow) because of the variety of color in its compounds. A very rare element (0.0001 ppm of Earth's crust), iridium is found in the naturally occurring **alloys** osmiridium (approximately 50% iridium) and iridiosmium (approximately 70% iridium) in Alaska and South Africa. It is obtained by igniting ammonium chloroiridate, $(NH_4)_3IrCl_6$, in hydrogen atmosphere. Its ground state electronic configuration is [Xe]4p^{14}5d^{7}6s^2.

metal: element or other substance the solid phase of which is characterized by high thermal and electrical conductivities

isotope: form of an atom that differs by the number of neutrons in the nucleus

Iridium is the densest of all elements and its **metal** is lustrous, silvery, and very hard. The metal has the face-centered cubic crystal structure. Iridium has two stable **isotopes**: ^{191}Ir (37.3%) and ^{193}Ir (62.7%).

IRIDIUM COMPLEXES WITH EXAMPLES

Oxidation States	Examples
(−I)	$K[Ir(PF_3)_4]$
(0)	$[Ir(NH_3)_5Br]Br$ (yellow)
(I)	$Ir(CO)Cl(PPh_3)_2$
(II)	$Ir(NO)Br_3(PPh_3)_2$ (μB = 1.34 BM)
(III)	$K_3[IrCl_6]$ (olive-green) diamagnetic
(IV)	$K_2[IrF_6]$ (red)
(V)	$K[IrF_6]$

Table 1. Iridium complexes with examples.

Iridium is extremely **inert** to acids, but reacts slowly with oxygen and **halogens** at high temperatures. It forms the fluoride compounds IrF_6, $(IrF_5)_4$, and IrF_4. There is some doubt of the existence of other halides with the composition IrX_4. The most stable halides are the trihalides. Compounds that have the composition $[IrX_6]^{2-}$ are strongly colored.

inert: incapable of reacting with another substance

halogen: element in the periodic family numbered VIIA (or 17 in the modern nomenclature) that includes fluorine, chlorine, bromine, iodine, and astatine

$Ir_2O_3 \cdot nH_2O$ (a brown solid) is obtained via the addition of alkali to $IrCl_6^{2-}$ in the presence of H_2O_2. This hydrated oxide is oxidized in air to $IrO_2 \cdot nH_2O$. IrO_2 (black), with **rutile** structure, is the product of the reaction of Ir with O_2 at approximately 1,100°C (2,012°F); it dissociates at higher temperatures (>1,100°C, or >2,012°F).

rutile: common name of titanium dioxide; also a common structural type for compounds with the general composition AB_2

Iridium may form complexes in its several **oxidation** states. Table 1 contains some examples of these complexes.

oxidation: process that involves the loss of electrons (or the addition of an oxygen atom)

Iridium oxide, IrO_2, is used in the fabrication of thin films for stable electrochromic materials and as an electrode material. Iridium metal is used in the manufacture of fountain pen points, airplane spark plugs, and hypodermic needles. SEE ALSO Inorganic Chemistry.

Lea B. Zinner

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Iron

MELTING POINT: 1,535°C
BOILING POINT: 2,750°C
DENSITY: 7.874 g/cm^3 (at 20°C)
MOST COMMON IONS: Fe^{2+}, Fe^{3+}

26
Fe
IRON
55.847

Iron, believed to have been introduced on Earth by meteors, was found in Egyptian tombs dating from 3500 B.C.E. The Hittites (in the area known today as Turkey) smelted iron from ore around 1500 B.C.E. From ancient times to the present, the major use of iron has been in the production of steel.

Elemental iron, the major element in Earth's core, is the fourth most abundant element in Earth's crust (about 5.0% by mass overall, 0.5%–5% in soils, and approximately 2.5 parts per billion in seawater.) In the crust, iron is found mainly as the oxide minerals hematite, Fe_2O_3, and magnetite, Fe_3O_4. Other common mineral forms are siderite, $FeCO_3$, and various forms of FeO(OH). Iron is an essential element in almost all living organisms. In the human body, its concentration ranges between 3 and 380 parts per million (ppm) in bone, 380–450 ppm in blood, and 20–1,400 ppm in tissue.

isotope: form of an atom that differs by the number of neutrons in the nucleus

metal: element or other substance the solid phase of which is characterized by high thermal and electrical conductivities

oxidation: process that involves the loss of electrons (or the addition of an oxygen atom)

ferrous: older name for iron in the +2 oxidation state

ferric: older name for iron in the +3 oxidation state

halogen: element in the periodic family numbered VIIA (or 17 in the modern nomenclature) that includes fluorine, chlorine, bromine, iodine, and astatine

Iron has a very stable nucleus and has fourteen known **isotopes**. Four isotopes, ^{54}Fe (5.9%), ^{56}Fe (91.72%), ^{57}Fe (2.1%), and ^{58}Fe (0.28%) make up essentially 100 percent of naturally occurring iron. Pure iron is a soft, white, lustrous **metal**. Elemental iron oxidizes in moist air but is stable in dry air. Finely divided elemental iron is pyrophoric. Iron dissolves in dilute mineral acid and in hot sodium hydroxide solution. Iron has seven **oxidation** states (–2, 0, +1, +2, +3, +4, and +6) with the +2, **ferrous** or Fe(II), and +3, **ferric** or Fe(III), states being the most common. With mild heating, iron reacts with the **halogens** and with sulfur, phosphorus, boron, carbon, and silicon to form a variety of compounds. SEE ALSO HEMOGLOBIN; INDUSTRIAL CHEMISTRY, INORGANIC.

Douglas Cameron

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Irradiated Foods

isotope: form of an atom that differs by the number of neutrons in the nucleus

metal: element or other substance the solid phase of which is characterized by high thermal and electrical conductivities

Gray: unit of radiation dose per second; 1 Gray = 1 J/kg

DNA: deoxyribonucleic acid—the natural polymer that stores genetic information in the nucleus of a cell

photon: a quantum of electromagnetic energy

Irradiation is the process of exposing a material to ionizing radiation whose source is photons (γ-rays, x rays), or high energy electrons. Commonly, γ-rays are produced by radioactive **isotopes** such as cobalt-60 and cesium-137. These isotopes have been approved for use in food because the γ-rays they produce have insufficient energy to induce radioactivity in foods. Conversely, electron beams are produced by electron accelerators, such as Van de Graaff generators or linear accelerators. The power limits for these machines are also regulated to no more than 10 million EV, to assure that they cannot induce radioactivity in foods. Finally, x rays are produced by the collision of high energy electrons, produced by linear accelerators, with a **metal** target. The amount of ionizing energy absorbed by a material is the dose, and this dose is measured in Grays (1 **Gray**, abbreviated Gy, equals 1 J/kg) or kiloGrays (kGy).

Irradiation destroys bacteria primarily by disrupting the chromosomal **DNA** in individual cells. A second mode of action is the "near-miss" theory, where a **photon** of energy passes very close to the DNA and forms a peroxide radical (from oxygen in the air) in the cell cytoplasm. The peroxide radical then oxidizes part of the DNA.

Purposes of Food Irradiation

The purpose of food irradiation is to improve the quality of the food being irradiated, either from a microbiological, physical, or **organoleptic** perspective. Very low doses (<1 kGy) are used to prevent sprouting in potatoes or delay the ripening of fruits. These doses can also be used to disinfect foods by killing insects in grains and fruits or inactivating parasites (trichinae) in meat. Slightly higher doses (1–5 kGy) can be used to pasteurize foods. Radiation **pasteurization**, or radurization, significantly reduces or eliminates bacteria of public health significance in the food while also decreasing the total number of bacteria in the food. As with pasteurization by heating, this reduction in the total number of bacteria in a food also results in an increase in the shelf life of the food. Finally, very high doses, on the order of 25 kGy or greater, can be used to sterilize foods. In practice, most of the current interest and research has focused on the low doses commonly used in pasteurization.

organoleptic: effect of a substance on the five senses

pasteurization: process of heating foods such as milk to destroy bacteria

One of the main interests in food irradiation is that it can be used as a "cold" pasteurization technique. Many food-borne disease bacteria, including *Salmonella*, *Escherichia coli* O157:H7, and *Listeria monocytogenes*, are very sensitive to irradiation. Although there are some variations in sensitivity among the previously listed bacteria, a dose range of 1.5–3.0 kGy is sufficient to eliminate all these bacteria as they naturally occur in foods.

An advantage of irradiation is that it can penetrate packaging material. Foods can be prepackaged and then irradiated, eliminating the potential for contamination during packaging. In addition, irradiation can be used as a replacement for many food additives that are used to inhibit bacterial growth. Irradiation can also be used as a quarantine treatment for imported fruits and vegetables, which eliminates the need for the use of toxic fumigants.

Irradiation can kill many disease-causing bacteria, including *E. coli, Listeria,* and salmonella. Irradiation can penetrate packaging, eliminating contamination introduced during the packaging process.

Consumer Concerns

vitamins: organic molecules needed in small amounts for the normal function of the body; often used as part of an enzyme catalyzed reaction

Consumer concerns about food irradiation fall into two broad categories: the first relating to the technology and the second relating to the quality of the food. The terms "radiation" and "radioactivity" have negative connotations to many individuals. There is still lingering doubt in the mind of some consumers regarding induced radiation. The radiation sources that the U.S. Food and Drug Administration (FDA) has approved for food irradiation cannot make the food radioactive. Another consumer concern relating to the quality of the irradiated food is that of nutrient loss. Irradiation does, in fact, reduce the levels of **vitamins** in foods, especially the B vitamins. Thiamine is particularly sensitive to irradiation, and substantial losses of this vitamin can occur in irradiated foods at high doses. However, vitamin losses occur with many food processes, including cooking and canning. There is no question that an irradiated food which is cooked will have a slightly lower vitamin content than an identical food which has not been irradiated prior to cooking. However, it is not anticipated that every food will be irradiated, and even if an individual specifically limited his or her consumption to irradiated products, there would still be sufficient vitamins in that individual's diet. The American Dietetics Association (ADA) has reviewed the nutritional changes caused by food irradiation and is on record as supporting the technology.

Toxicity

The ultimate consumer concern with any new food process is, "Is the food safe to eat?" A joint committee of the Food and Agriculture Organization (FAO), the International Atomic Energy Agency, and the World Health Organization (WHO) evaluated all available studies on the wholesomeness of irradiated food. The final report concluded that the irradiation of any food commodity causes no toxicological hazard and hence toxicological testing of foods treated in this manner is no longer required. Many toxicological studies have been conducted over the years, but one of the most comprehensive was a multigenerational study conducted in the United States during the 1970s, in which five different species of animals and insects were fed irradiation-sterilized (58 kGy) chicken as a major component in their diet. The results of these studies, including all the original histology slides, were completely reevaluated by the FDA during its consideration of the petition to irradiate poultry. After more than two years of evaluation, the FDA concurred with the conclusions of the original study and issued regulations on poultry irradiation. In addition, during this same time period the American Medical Association (AMA) reviewed the toxicological data; it has publicly supported food irradiation. SEE ALSO AGRICULTURAL CHEMISTRY; RADIATION; RADIOACTIVITY; TOXICITY.

James S. Dickson

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Isomerism

The term **"isomer"** (*iso* from the Greek meaning same and *meros* meaning part) describes the relationship between molecular arrangements that, although differing in chemical or physical properties, have a level of commonality (have the "same parts"). There are two distinct levels of commonality used to describe molecular structure: one that excludes and one that includes three-dimensional considerations. The level of comparison that excludes three-dimensionality is comprised of substances having the same set of atoms but differing in how they are connected. These substances are known as **constitutional isomers**. The constitution of molecules (number, kind, and connectivity of atoms) may be represented by a two-dimensional "map" in which the interatomic linkages are indicated. There are two constitutional isomers for the molecular formula C_2H_6O: ethanol and dimethyl ether. The difference in connectivity, which is not evident in the empirical formula C_2H_6O, can be represented by typographical line formulas, CH_3CH_2OH for ethanol and CH_3OCH_3 for dimethyl ether, or in structural representations (see Figure 1). As the number and kind of atoms in substances increases, the number of constitutional isomers increases.

isomer: molecules with identical compositions but different structural formulas

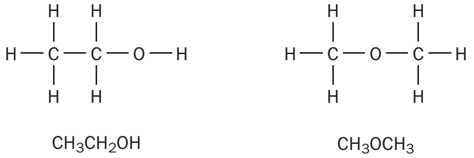
constitutional isomer: form of a substance that differs by the arrangement of atoms along a molecular backbone

Chemical reactions in which one isomer is converted to another are called isomerizations. An intramolecular Diels–Alder reaction (see Figure 2) is an example of an isomerization reaction in which the level of difference is that of connectivity. An isomerization that involves a rapid **equilibrium** between connectivities that cannot be easily isolated from one another is called a tautomerization (see Figure 3). Note that the number and kind of atoms remains the same on both sides of the chemical equation, and that there is only one compound involved.

equilibrium: condition in which two opposite reactions are occurring at the same speed, so that concentrations of products and reactants do not change

History

The concept of constitutional isomerism was a significant advance in the history of modern chemistry, and especially in the development of organic chemistry. By the late 1700s only a few pure substances had been isolated via the study of "animal" and "vegetable" chemistry, and many of these by a single individual, Carl Wilhelm Scheele (1742–1786). Due to the extensive variety in organic compounds, each new substance presented a new elemental composition, which matched the generalized observation from "mineral" chemistry. As the number of isolated organic compounds increased during the early 1800s, the identification of different substances

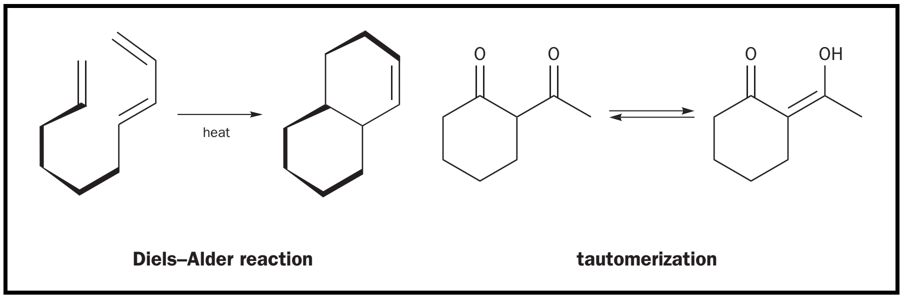


CH_3CH_2OH CH_3OCH_3

ethanol **dimethyl ether**

Figure 1.

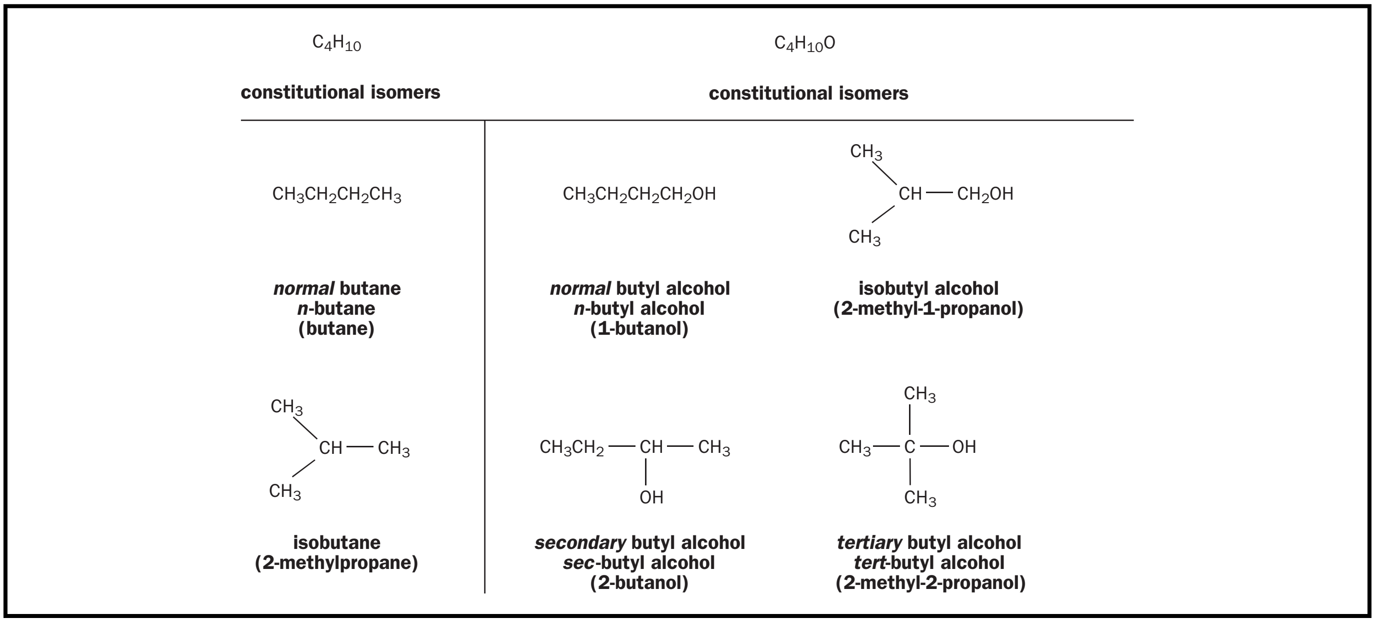
Figures 2–3.



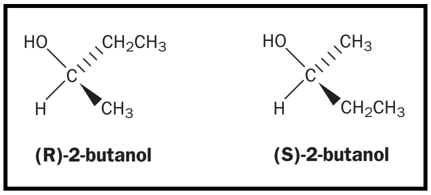
having the same elemental composition was inevitable. In his 1830 *History of Chemistry*, Thomas Thomson wrote (p. 302) that "[Berzelius] applied the [atomic] theory also to the vegetable kingdom by analyzing several of the vegetable acids, and showing their atomic constitution. But here a difficulty occurs, which in the present state of our knowledge, we are unable to surmount. There are two acids . . . that are composed of exactly the same kind of atoms. . . . Now how are we to account for this [striking difference in properties]? Undoubtably by the different ways in which the atoms are arranged in each." Thomson then drew different arrangements (on paper) of the atomic symbols used at the time (those of John Dalton), as a way to explain why two acids with the same elemental composition could have different physical and chemical properties.

Up until the early nineteenth century, it was generally believed that those chemical substances found in living organisms possessed a particular vital force associated with living things, and that these substances required living systems in order to be produced. The belief was that nowhere else in nature except in living systems could one find these compounds. Friedrich Wöhler (1800–1882) is universally credited with the observation of isomerization that led to the decline of the idea of vitalism. In 1828 Wöhler synthesized a sample of urea, $(NH_2)_2C{=}O$ (also CH_4N_2O), that was

Figure 4. Constitutional isomers for C_4H_{10} and $C_4H_{10}O$.



indistinguishable from the urea isolated from urine. He prepared this "animal" substance from the clearly inorganic (mineralogical) starting material ammonium cyanate, NH_4 (+) NCO(−) (also CH_4N_2O), which results from combining ammonium chloride and silver cyanate. In *The Development of Modern Chemistry*, Aaron J. Ihde (p. 165) points out that the preparation of urea from inorganic starting materials had been conducted earlier, by both Wöhler, in 1824, and Humphry Davy, in 1811, but that their achievements were not recognized for what they were at the time. The concept of isomerism is central to structural chemistry, and this concept is beautifully encapsulated in the title of a book by Nobel laureate Roald Hoffmann, *The Same and Not the Same.*



(R)-2-butanol **(S)-2-butanol**

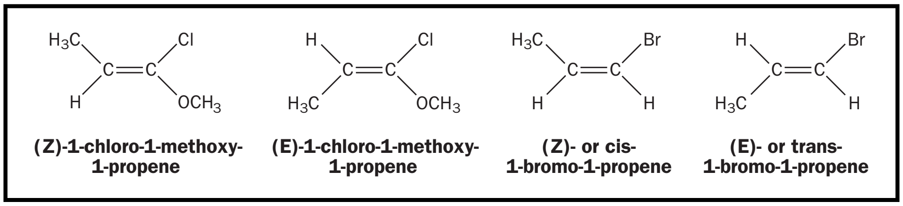
Figure 5.

Nomenclature

The early development of a systematic nomenclature for organic compounds reflected structural isomeric relationships. A few of the terms have persisted: "normal" or "n-" to indicate a straight chain of atoms; "iso" as a prefix derived from the word "isomer" to indicate the attachment of a methyl group on the penultimate carbon of a straight chain; "tertiary," "tert-," or "t-" to indicate an arrangement in which three alkyl groups are attached to a common site; and "secondary" or "sec-" to indicate that there are two alkyl groups. Examples of common usage are provided in Figure 4 (the contemporary standard usage is included parenthetically).

Stereoisomerism

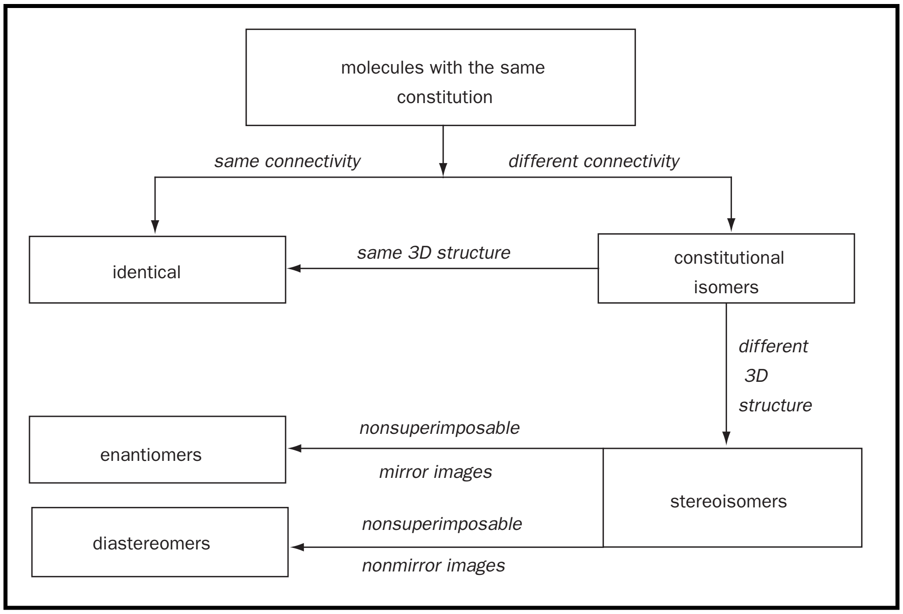
The second level of isomeric comparison includes substances that have the same connectivity but differ in their three-dimensional geometrical arrangements. The study of the resulting relationships is called stereochemistry. Two categories exist for comparing different three-dimensional geometries: configuration and conformation. Because there is an empirical component to these terms, a universally unambiguous distinction between configurational stereoisomers (sometimes simply referred to as stereoisomers) and conformational stereoisomers (sometimes simply referred to as conformations or conformers) has not emerged. There is a general understanding, however, that stereoisomers are geometrical forms that are distinct enough to be isolated under normal conditions, whereas conformers are geometrical forms that interconvert under the same conditions. Some examples will help to clarify this distinction. Tetravalent atoms bearing four different atoms or atomic groupings can occur in two different geometrical forms. The carbon atom with the OH group in 2-butanol (see Figure 4) demonstrates this. The two (and only two) different arrangements of 2-butanol are shown in Figure 5. Both of these molecules have the 2-butanol connectivity, but their three-dimensionality must be additionally labeled in order to give these two different molecules different names. Using a system that is based on assigning



(Z)-1-chloro-1-methoxy-1-propene **(E)-1-chloro-1-methoxy-1-propene** **(Z)- or cis-1-bromo-1-propene** **(E)- or trans-1-bromo-1-propene**

Figure 6.

Figure 7. Schematic relationship between isomers.



priorities to the four different groups, called the Cahn–Ingold–Prelog rules, one of two unique geometrical labels, namely "R" or "S," can be assigned to the three-dimensional geometry of such an atom. "R" and "S" come from the Latin terms *rectus* and *sinester*, meaning "to the right" and "to the left," respectively.

The greater the number of these tetrahedral centers with four different groups that there are in a molecule, the greater the number of stereoisomers. For the most part, this is a simple exercise in probability and statistics. With two such centers, there are four stereoisomers possible (2 geometries at the one center × 2 at the second = 4), and with three such centers there are eight stereoisomers (2 × 2 × 2 = 8).

There are other molecular subunits that can give rise to stereoisomers. Double bonds that bear different groups at both ends, for example, give rise to two distinctly different stereoisomers that do not easily interconvert under normal conditions. Using the Cahn–Ingold–Prelog rules once again, geometrical labels of "E" and "Z" can be assigned to these geometrical arrangements. "E" and "Z" come from the German terms *entgegen* and *zusammen*, meaning "apart" and "together," respect ively. In some cases, in which there is one hydrogen atom at each end, the labels "cis" and "trans" may also be used (see Figure 6).

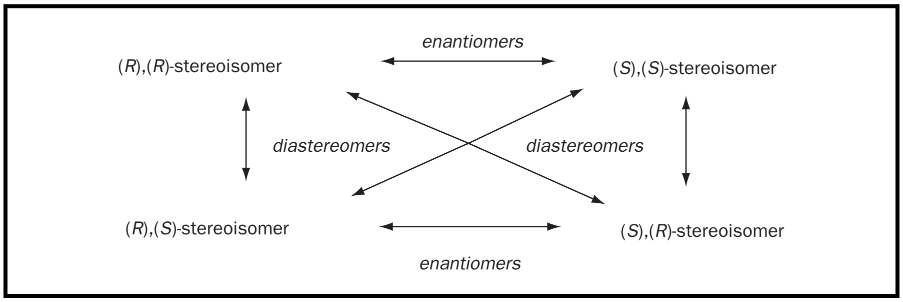
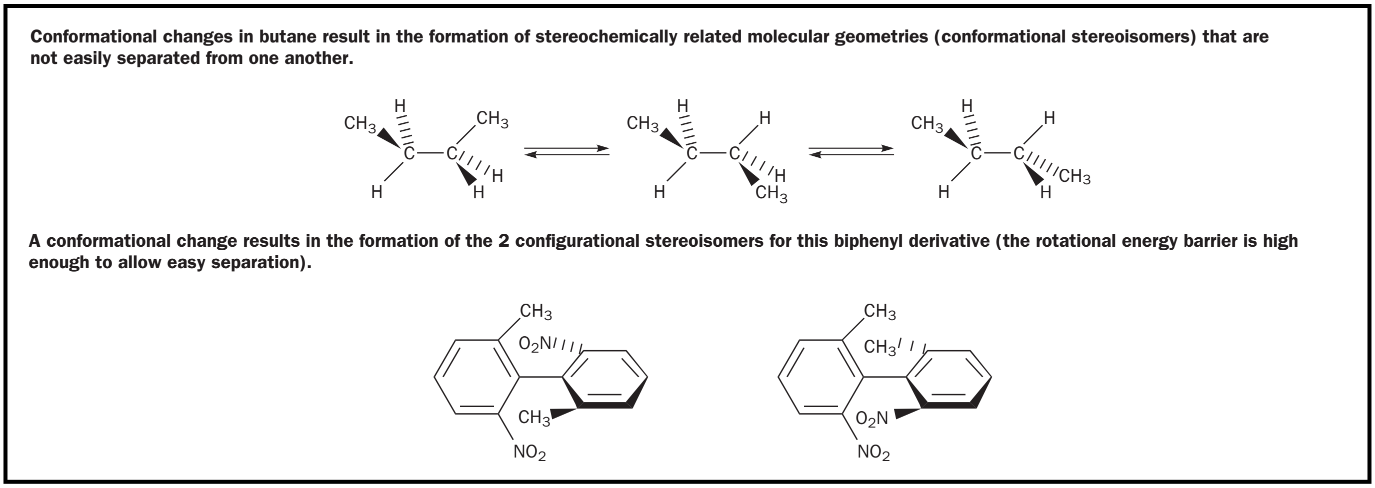


Figure 8.



Conformational changes in butane result in the formation of stereochemically related molecular geometries (conformational stereoisomers) that are not easily separated from one another.

A conformational change results in the formation of the 2 configurational stereoisomers for this biphenyl derivative (the rotational energy barrier is high enough to allow easy separation).

Figure 9. Conformational changes.

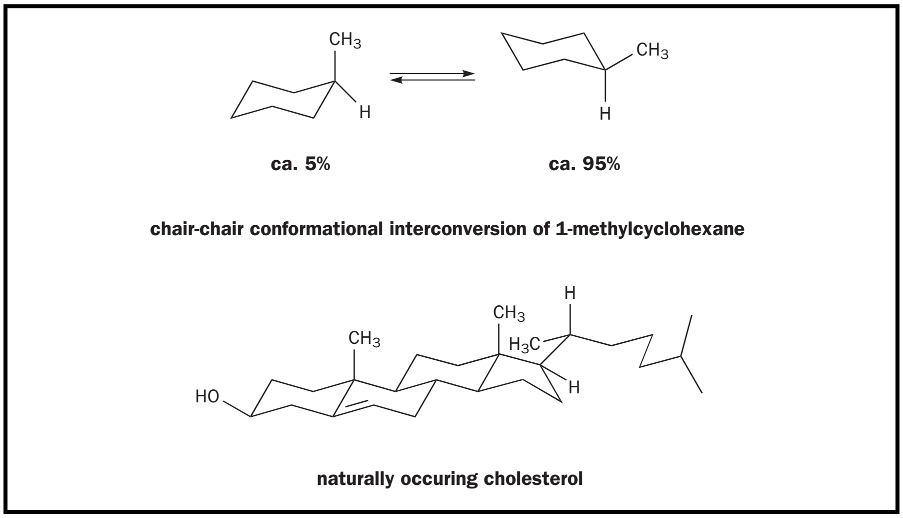
Stereoisomers: Enantiomers and Diastereomers

The two categories into which stereoisomers can be placed are absolutely distinctive in definition. Two stereoisomers that are nonsuperimposable mirror images are called enantiomers. The only other category is defined negatively. Stereoisomers that are not enantiomers are called diastereomers. (See Figure 7.)

Molecules with a single stereocenter as the only source of configurational stereoisomerism can exist as one of two enantiomers; no configurational diastereomers are possible. Molecules with two dissimilar stereocenters can exist as one of four stereoisomers. Figure 8 outlines the relationships among these four stereoisomers.

Conformers

According to Ernest L. Eliel and Samuel H. Wilen in *Stereochemistry of Organic Compounds* (1994, p. 102), configurational stereoisomers result from "arrangments of atoms in space of a molecule with a defined constitution without regard to arrangements that differ only by rotation about one or



chair-chair conformational interconversion of 1-methylcyclohexane

naturally occuring cholesterol

Figure 10.

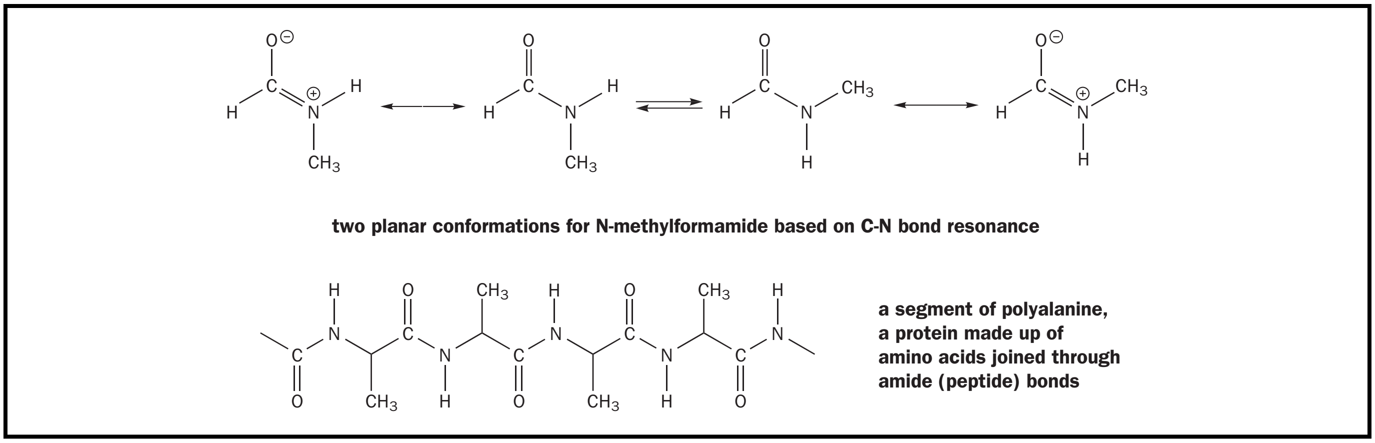


Figure 11. The chemistry of amide bonds involves restricted rotation.

more single bonds, providing that such a rotation is so fast as not to allow isolation of the species so differing." Conformational stereoisomers are then taken to be the result of such single bond rotations. Every single bond that has atoms with some identifiable geometry exists in a full range of molecular geometrical shapes based on rotation around that bond. Some examples are shown in Figure 9. In the first example, the bond rotation of the central bond of butane creates a series of molecular geometries that cannot be isolated or separated from each other. On the other hand, the Eliel and Wilen definition is well illustrated by the second example. The single bond between the two benzene rings has undergone only a 180° rotation in defining the relationship between the two structures (a conformational change), yet this creates two different molecules (stereoisomers), because under normal conditions these two molecular geometries are not easily interconverted, and these two represent separable molecules. It is not easy to predict when two separable molecules are going to be possible; it is determined empirically.

The effects of the overall molecular geometry of a molecule were recognized as contributing to chemical reactivity in the 1950s. Substituted cyclohexanes were among the first systems that could be explained by conformational analysis. These structural units appear in many different (and biologically significant) molecules. Methylcyclohexane, for example, exists as a roughly 95:5 mixture of two forms differing in stability based on the bad collisional interaction that exists for the methyl group when it lies closer to the rest of the ring. Notice how this molecular shape, called a **chair**

chair conformation: arrangement of atoms in a cycle structure (usually a six-membered ring) that appears to be arranged like a chair (as opposed to the other conformation which is described as a "boat")

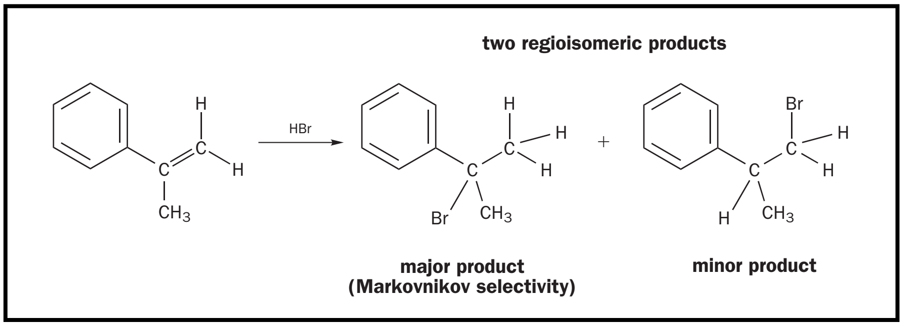


Figure 12.

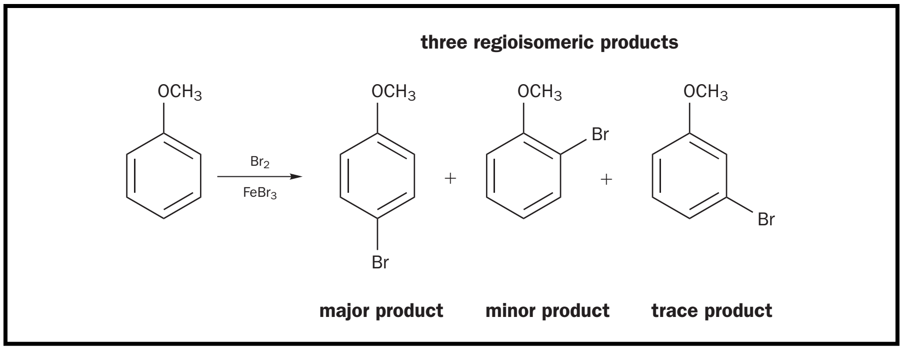


Figure 13.

conformation, recurs in the more complex cholesterol molecule (see Figure 10).

Rotamers

In general, single bonds can undergo free rotation, while double bonds cannot. Because of the resonance phenomenon, some bonds have character that puts them partially between single and double bonding. Sometimes the partial double bond is strong enough to prevent fast bond rotation but weak enough to permit both possible geometrical isomers to be present. The amide **functional group**, which in biochemistry is called the peptide bond in proteins, demonstrates this property (see Figure 11).

functional group: portion of a compound with characteristic atoms acting as a group

Regioisomers

Another type of isomerism is produced as a result of the different outcomes of chemical reactions in which there are different orientations or sites to choose from. For example, when addition reactions between unsymmetrical **reagents** and unsymmetrical double or triple bonds occur, two outcomes are possible. As part of the original observations of this chemistry, wherein one of the atoms added was a hydrogen and the other was some distinctive, nonhydrogen atom, the placement of this distinctive atom was said to occur at one region or other of the molecule, hence the formation of regioisomers (see Figure 12). Based on the mechanism of the chemical reaction, the selectivity for one of these regioisomers forming faster than the other can be predicted. With the addition of simple mineral acids, for example, the product derived from a faster protonation giving a more stable **intermediate** is referred to as the Markovnikov regioselectivity, after the nineteenth-century Russian chemist who made the observations (see Figure 12).

reagent: chemical used to cause a specific chemical reaction

intermediate: molecule, often short-lived, that occurs while a chemical reaction progresses but is not present when the reaction is complete

Regioselectivity in the formation of regioisomers is also observed in electrophilic aromatic substitution reactions. In the case of monosubstituted benzene derivatives, there are three possible regiosomeric products that form at different rates, based on the mechanism of the reaction (see Figure 13). SEE ALSO Berzelius, Jöns Jakob; Chirality; Dalton, John; Davy, Humphry; Molecular Structure; Scheele, Carl; Wöhler, Friedrich.

Brian P. Coppola

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Julian, Percy

AMERICAN CHEMIST
1899–1975

Percy Lavon Julian, the grandson of slaves, developed many useful products from soybeans, including cortisone. He was born in Montgomery, Alabama, on April 11, 1899. His father, James Sumner Julian, was a railway clerk, and his mother, Elizabeth Lena (Adams) Julian, a schoolteacher.

Julian attended public schools in Montgomery. After he was admitted to DePauw University, his family moved with him to Greencastle, Indiana, to enable them to give him their full support. At DePauw his interest in science evolved into a desire to become a research organic chemist. Julian graduated at the top of his class with a bachelor's degree in chemistry in 1920. He was class valedictorian and was elected to Phi Beta Kappa.

Julian taught organic chemistry for two years at Fisk University in Nashville, Tennessee. He then, with the help of Professor William M. Blanchard at DePauw, obtained a graduate research fellowship at Harvard University. He earned a master's degree there in one year, again finishing at the top of his class. He remained at Harvard three more years, as a research assistant, supporting himself with minor fellowship positions and odd jobs outside the university. His application for a teaching assistantship at Harvard was repeatedly rejected on the grounds that the students would not respect a "Negro" instructor.

In 1926 Julian joined the faculty of the West Virginia School for Negroes (later West Virginia State College) at Institute, West Virginia. A year later he became an associate professor of chemistry at Howard University in Washington, D.C., where he quickly rose to the positions of full professor and department head.

Julian had become interested in the chemistry of natural substances and was very eager to do original research in that field. Frustrated in his efforts to pursue doctoral studies in the United States, he obtained a fellowship for graduate study at the University of Vienna, Austria, where he worked and studied indole **alkaloids** under the tutelage of Professor Ernst Spaeth. He earned a Ph.D. from the University of Vienna in 1931.

Upon Julian's return to the United States, DePauw University offered him a faculty position and research support. His first project was the total **synthesis** of **physostigmine**, an indole alkaloid extracted from the Calabar bean, used in the treatment of glaucoma. Sir Robert Robinson at Oxford University in England was also working on this synthesis. Julian achieved the synthesis of physostigmine, and showed that Robinson's hypotheses about its structure were wrong.

Having also found **stigmasterol** among the substances in the Calabar bean, Julian directed his research efforts toward using this **sterol** as the start-

alkaloid: alkaline nitrogen-based compound extracted from plants

synthesis: combination of starting materials to form a desired product

physostigmine: alkaloid derived from the leaves of the Calabar bean, formula $C_{15}H_{12}N_3O_2$; salts are used for anticholinesterase activity

stigmasterol: sterol found in soybeans, $C_{29}H_{48}O$

sterol: steroid containing an alcohol group; derived from plants or animals; e.g., cholesterol ing point for the synthesis of the sex hormones. Because stigmasterol is readily available from soybean oil, Julian wrote to the Glidden Company, a major manufacturer of soybean oil products, to request a 5-gallon sample of the oil to use as his starting point. The request elicited a telephone call from Glidden, offering Julian the position of director of research of Glidden's Soya Products Division in Chicago.

Julian worked for Glidden for seventeen years, developing several new products from soybeans. He mapped out commercially viable syntheses of **progesterone**, testosterone, and cortisone from soya sterols. From soya protein he developed "Aero-Foam," a fire extinguishing foam for oil and gasoline fires, which saw use by the U.S. armed forces during World War II.

progesterone: steroid found in the female reproductive system: formula $C_{21}H_{30}O_2$

In 1953 Julian resigned from Glidden to establish his own laboratory in Franklin Park, Illinois. As director of the Julian Research Institute and president of Julian Associates, Inc., he continued work on steroid chemistry and returned to his studies of indole alkaloids. In 1974 Julian became ill, and it was necessary for him to scale back his activities. He died on April 19, 1975.

Julian's scientific work generated about 100 technical papers and more than 200 patents. He received nineteen honorary degrees, was a trustee at six colleges and universities, and was active in the Chicago Urban League, the National Association for the Advancement of Colored People (NAACP), and the Mental Health Association of Greater Chicago.

The man who had stoked furnaces to support himself at Harvard was the first African American to serve as a faculty member of a non-Negro college and to achieve a supervisory research position within a major American corporation. When, in 1950, Julian became the first African American to purchase a home in all-white Oak Park, Illinois, he and his family became the objects of racist threats and even attacks. As in his professional career, Julian stood firm, and won the respect of his new neighbors.

Julian attributed his success in life and in his professional career to the motivation he received from his father, who taught him that he should not be satisfied with being merely good, when he had the ability to be the very best. SEE ALSO CORTISONE; MEDICINAL CHEMISTRY.

Lyman R. Caswell

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Glossary

acetylcholine: neurotransmitter with the chemical formula $C_7H_{17}NO_3$; it assists in communication between nerve cells in the brain and central nervous system

acid rain: precipitation that has a pH lower than 5.6; term coined by R. A. Smith during the 1870s

activation analysis: technique that identifies elements present in a sample by inducing radioactivity through absorbtion of neutrons

adenine: one of the purine bases found in nucleic acids, $C_5H_5N_5$

adenosine triphosphate (ATP): molecule formed by the condensation of adenine, ribose, and triphosphoric acid, HOP(O)OH–O–(O)OH–OP(O)OH–OH; it is a key compound in the mediation of energy in both plants and animals

adrenalin: chemical secreted in the body in response to stress

alchemy: medieval chemical philosophy having among its asserted aims the transmutation of base metals into gold

aldehyde: one of the characteristic groups of atoms in organic compounds that undergoes characteristic reactions, generally irrespective of where it occurs in the molecule; the RC(O)H functional group

aliphatic: having carbon atoms in an open chain structure (as an alkane)

aliquot: specific volume of a liquid used in analysis

alkaloid: alkaline nitrogen-based compound extracted from plants

alloy: mixture of two or more elements, at least one of which is a metal

α subunit: subunit that exists in proteins that are composed of several chains of amino acids, the first unit in the "counting" of the units

α-particle: subatomic particle with 2+ charge and mass of 4; a He nucleus

amalgam: metallic alloy of mercury and one or more metals

amine functional group: group in which nitrogen is bound to carbon in an organic molecule in which two other groups or hydrogen atoms are bound to nitrogen; major component of amino acids

amino acid residue: in a protein, which is a polymer composed of many amino acids, that portion of the amino acid that remains to become part of the protein

amino acid sequence: twenty of the more than five hundred amino acids that are known to occur in nature are incorporated into a variety of proteins that are required for life processes; the sequence or order of the amino acids present determines the nature of the protein

amphetamine: class of compounds used to stimulate the central nervous system

anabolism: metabolic process involving building of complex substances from simpler ones, using energy

analgesic: compound that relieves pain, e.g., aspirin

androgen: group of steroids that act as male sex hormones

angiotensin: chemical that causes a narrowing of blood vessels

anhydrous compound: compound with no water associated with it

anion: negatively charged chemical unit, like $Cl-$, $CO_{32}-$, or NO_3-

anthcyanin: antioxidant flavanoid that makes raspberries red and blueberries blue

antibody: protein molecule that recognizes external agents in the body and binds to them as part of the immune response of the body

anticoagulant: molecule that helps prevent the clotting of blood cells

antiscorbutic: substance that has an effect on scurvy

apoenzyme: the protein part of an enzyme that requires a covalently bound coenzyme (a low molecular weight organic compound) or a cofactor (such as a metal ion) for activity

aqueous solution: homogenous mixture in which water is the solvent (primary component)

aromatic: having a double-bonded carbon ring (typified by benzene)

asparagine residue: amino acid asparagine unit as it occurs in a polypeptide chain

atomic mass units: unit used to measure atomic mass; 1/12 of the mass of a carbon-12 atom

atomic number: the number of protons in an atomic nucleus, expressed in terms of electric charge; it is usually denoted by the symbol Z

atomic orbital: mathematical description of the probability of finding an electron around an atom

atomic spectrum: electromagnetic array resulting from excitement of a gaseous atom

atomic theory: concept that asserts that matter is composed of tiny particles called atoms

atomic weight: weight of a single atom of an element in atomic mass units (amu)

attraction: force that brings two bodies together, such as two oppositely charged bodies

axial bond: covalent bond pointing along a molecular axis

azo dye: synthetic organic dye containing a –N=N– group

bacteriophage multiplication: process by which immune system cells responsible for battling bacterial infections reproduce

basal metabolism: the process by which the energy to carry out involuntary, life-sustaining processes is generated.

β subunit: subunit that exists when two or more polypeptide chains associate to form a complex functional protein, the chains are referred to as "subunits"; these subunits are often identified as α, β, etc.

biological stain: dye used to provide contrast among and between cellular moieties

biomass: collection of living matter

biosynthesis: formation of a chemical substance by a living organism

boat conformation: the arrangement of carbon atoms in cyclohexane, C_6H_{12}. In which the spatial placement of the carbon atoms resembles a boat with a bow and a stern

brine: water containing a large amount of salts, especially sodium chloride (NaCl)

Brownian motion: random motion of small particles, such as dust or smoke particles, suspended in a gas or liquid; it is caused by collisions of the particle with gas or solvent molecules which transfer momentum to the particle and cause it to move

calc: calcium carbonate

calcine: to heat or roast to produce an oxide (e.g., CaO from calcite)

capacitor plate: one of several conducting plates, or foils, in a capacitor, separated by thin layers of dielectric constant, an insulating material

carboxylate: structure incorporating the –COO– group

carboxyl group: an organic functional group, –C(O), found in aldehydes, ketones, and carboxyl acids.

carboxylic acid: one of the characteristic groups of atoms in organic compounds that undergoes characteristic reactions, generally irrespective of where it occurs in the molecule; the $–CO_2H$ functional group

catabolism: metabolic process involving breakdown of a molecule into smaller ones resulting in a release of energy

catalysis: the action or effect of a substance in increasing the rate of a reaction without itself being converted

catalyst: substance that aids in a reaction while retaining its own chemical identity

catalytic conversion: catalytic oxidation of carbon monoxide and hydrocarbons in automotive exhaust gas to carbon dioxide and water

cell culture: artificially maintained population of cells, grown in a nutrient medium and reproducing by asexual division

cephalosporin C: family of antibiotics obtained from a fungus acting in a manner similar to penicillin

chain of custody: sequence of possession through which evidentiary materials are processed

chair conformation: arrangement of atoms in a cycle structure (usually a six-membered ring) that appears to be arranged like a chair (as opposed to the other conformation which is described as a "boat")

chemical-gated: of a membrane protein whose action to open a pore in the membrane occurs only after a substrate has been binded to the protein or a cofactor

chlorofluorocarbon (CFC): compound containing carbon, chlorine, and fluorine atoms that remove ozone in the upper atmosphere

chlorophyll: active molecules in plants undergoing photosynthesis

chromatography: the separation of the components of a mixture in one phase (the mobile phase) by passing in through another phase (the stationary phase) making use of the extent to which the components are absorbed by the stationary phase

chromophore: part of the molecule that yields characteristic colors

cladding: protective material surrounding a second material, which is frequently tubes filled with uranium dioxide pellets in a nuclear reactor

cleave: split

cobrotoxin: polypeptide toxin containing sixty-two residues that is found in the venom of cobras

code: mechanism to convey information on genes and genetic sequence

cofactor: inorganic component that combines with an apoenzyme to form a complete functioning enzyme

coherent mass: mass of particles that stick together

color fastness: condition characterized by retention of colored moieties from a base material

combustion: burning, the reaction with oxygen

competitive inhibitor: species or substance that slows or stops a chemical reaction

complementarity: basis for copying the genetic information, where each nucleotide base has a complementary partner with which it forms a base-pair

congener: an element or compound belonging to the same class

constitutional isomer: form of a substance that differs by the arrangement of atoms along a molecular backbone

contact activity: process involving the touching of different surfaces

contraction: the shortening of a normal trend of a quantity

coordinate covalent bond: covalent bond in which both of the shared electrons originate on only one of the bonding atoms

coordination chemistry: chemistry involving complexes of metal ions surrounded by covalently bonded ligands

corrosive gas: gas that causes chemical deterioration

covalent bond: bond formed between two atoms that mutually share a pair of electrons

crystal lattice: three-dimensional structure of a crystaline solid

crystallization: process of producing crystals of a substance when a saturated solution in an appropriate solvent is either cooled or some solvent removed by evaporation

culture: living material developed in prepared nutrient media

cyanobacterium: eubacterium sometimes called "the blue-green alga"; it contains chlorophyll (the pigment most abundant in plants), has very strong cell walls, and is capable of photosynthesis

cyclopentadienyl ring: five-membered carbon ring containing two C–C double bonds; formula C_5H_6

cysteine residue: sulfhydryl-containing cysteine unit in a protein molecule

cytosine: heterocyclic, pyrimidine, amine base found in DNA

dedifferentiation: the opposite of the biological process of differentiation by which a relatively unspecialized cell undergoes a progressive change to a more specialized form or function

degradative: relating to or tending to cause decomposition

degrade: to decompose or reduce the complexity of a chemical

delocalized: of a type of electron that can be shared by more than one orbital or atom

denitrification: process of removing nitrogen

density-functional theory: quantum mechanical method to determine ground states

depolarization: process of decreasing the separation of charge in nerve cells; the opposite of hyperpolarization

deterministic: related to the assumption that all events are based on natural laws

deuteron: nucleus containing one proton and one neutron, as is found in the isotope deuterium

dialcohol: organic molecule containing two covalently-bonded –OH groups

diamagnetic: property of a substance that causes it to be repelled by a magnetic field

diamine: compound, the molecules of which incorporate two amino groups (–NH_2) in their structure, such as 1,2 diamino ethane (sometimes called ethylenediamine) and the three diamine benzene compounds

dibasic acid: acidic substance that incorporates two or more acidic hydrogen atoms in one molecule, such as sulfuric (H_2SO_4) and phosphoric (H_3PO_4) acids

dihydroxy compound: compound with molecules that incorporate two hydroxyl groups (–OH) in their structure, such as 1,2 dihydroxy ethane (sometimes called glycol) and the three dihydroxy benzene compounds

directing effect: ability of a functional group to influence the site of chemical reaction, such as substitution, for a molecule

discharge display tube: glass tube containing gas at low pressure through which a beam of electrons is passed

disperse system: two-phase system in which one phase, the disperse phase, is distributed in the second phase, the dispersion medium

disulfide bond: bond in a complex substance that involves two bonding sulfur atoms, –S–S–

disulfide bridge: covalent –S–S– linkage that provides cross-links in protein molecules

DNA: deoxyribonucleic acid—the natural polymer that stores genetic information in the nucleus of a cell

dope: to add a controlled amount of an impurity to a very pure sample of a substance, which can radically change the properties of a substance

drug resistance: ability to prevent the action of a particular chemical substance

ductile: property of a substance that permits it to be drawn into wires

Eighteen Electron Rule: rule noting that coordination complexes with eighteen electrons are stable; electrons from both metal species and ligand donor species are counted

electrolyte solution: a liquid mixture containing dissolved ions

electron correlation error: quantum mechanical method for studying atoms, ions, or molecules

electronegative: capable of attracting electrons

electrophoresis: migration of charged particles under the influence of an electric field, usually in solution; cations, the positively charged species, will move toward the negative pole and anions, the negatively charged species, will move toward the positive pole

electrostatic interaction: force that arises between electrically charged particles or regions of particles

elemental analysis: determination of the percent of each atom in a specific molecule

emulsifier: substance that stabilizes the formation of an emulsion—normally it contains molecules with both polar and non-polar functional groups

emulsion: immiscible two-phase mixture in which one phase is dispersed (as small droplets) in the other phase

enantiomorphic shape: mixture of molecules with the same molecular formulas but different optical characteristics

endohedral: descriptive term for a point within a three-dimensional figure

endoplasmic reticulum: internal membrane system that forms a net-like array of channels and interconnections of organelles within the cytoplasm of eukaryotic cells

Equation of State for Ideal Gases: mathematical statement relating conditions of pressure, volume, absolute temperature, and amount of substance; $PV = nRT$

equatorial bond: covalent bond perpendicular to a molecular axis

equilibrium: condition in which two opposite reactions are occurring at the same speed, so that concentrations of products and reactants do not change

erythromycin: antibiotic used to treat infections

ester: organic species containing a carbon atom attached to three moieties: an O via a double bond, an O attached to another carbon atom or chain, and an H atom or C chain; the R(C=O)OR functional group

esterification: chemical reaction in which esters (RCO_2R_1) are formed from alcohols (R_1OH) and carboxylic acids (RCO_2R')

estrogen: female sex hormone

eukaryotic cell: cell characterized by membrane-bound organelles, most notably the nucleus, and that possesses chromosomes whose DNA is associated with proteins

excitatory: phenomenon causing cells to become active

excitatory neurotransmitter: molecule that stimulates postsynaptic neurons to transmit impulses

exclusion principle: principle that states that no two electrons can have the same four quantum numbers

excrete: to eliminate or discharge from a living entity

expressed: made to appear; in biochemistry—copied

extracellular matrix: entity surrounding mammalian tissue cells, also called connective tissue; composed of structural proteins, specialized proteins, and proteoglycans

face centered cubic structure: close-packed crystal structure having a cubic unit cell with atoms at the center of each of its six faces

feedstock: mixture of raw materials necessary to carry out chemical reactions

Fermi conduction level: vacant or partially occupied electronic energy level resulting from an array of a large number of atoms in which electrons can freely move

ferric: older name for iron in the +3 oxidation state

ferrous: older name for iron in the +2 oxidation state

fibril: slender fiber or filament

fission: process of splitting of an atom into smaller pieces

fissionable: of or pertaining to unstable nuclei that decay to produce smaller nuclei

5′ end: situation in nucleic acids in which the phosphate group is attached at the fifth carbon atom from where the base is attached

folic acid: pteroylglutamic acid; one of the B complex vitamins

formaldehyde: name given to the simplest aldehyde HC(O)H, incorporating the –C(O)H functional group

fractional distillation: separation of liquid mixtures by collecting separately the distillates at certain temperatures

fulcrum: prop or support to an item as in a lever

functional group: portion of a compound with characteristic atoms acting as a group

galactose: six-carbon sugar

galvanic: relating to direct current electricity, especially when produced chemically

galvanometer: instrument used to detect and measure the strength of an electric current

gas density: weight in grams of a liter of gas

glucocorticoid: class of hormones that promotes the breakdown of proteins to make amino acids available for gluconeogenesis; this elevates the blood sugar level and leads to glycogen synthesis in the liver

glucose: common hexose monosaccharide; monomer of starch and cellulose; also called grape sugar, blood sugar, or dextrose

golgi apparatus: collection of flattened stacks of membranes in the cytoplasm of eukaryotic cells that function in the collection, packaging, and distribution of molecules synthesized in the cell

gram negative: bacteria that do not retain their color when exposed to basic dyes such as crystal violet and then exposed to organic solvents; named after Danish bacteriologist Hans Christian Joachim Gram

gram positive: bacteria that retain their color when exposed to basic dyes such as crystal violet and then exposed to organic solvents; named after Danish bacteriologist Hans Christian Joachim Gram

Gray: unit of radiation dose per second; 1 Gray = 1 J/kg

greenhouse effect: presence of carbon dioxide in the atmosphere prevents heat from escaping, thereby raising Earth's temperature

Griess reagent: solution of sulfanilic acid and a-naphthylamine in acetic acid; reagent for nitrites

guanine: heterocyclic, purine, amine base found in DNA

halogen: element in the periodic family numbered VIIA (or 17 in the modern nomenclature) that includes fluorine, chlorine, bromine, iodine, and astatine

heavy metal: by convention, a metal with a density greater than 5 g/cm^3; 70 elements are thus classified as heavy metals

helix: in the shape of a spiral or coil, such as a corkscrew

heme group: functional group formed by an iron atom interacting with a heterocyclic ligand called a porphyrin

hemiacetal: relating to organic compounds formed from an alcohol and a carbonyl-containing molecule

hemlock: poisonous herb of the genus Conium

Hippocrates: Greek physician of fifth century B.C.E. known as the "father of medicine"

homogeneous: relating to a mixture of the same materials

homogeneous solution: mixture of molecules that forms a single phase (solid, liquid, or gas)

hormonal signaling: collective processes by which hormones circulate in the blood stream to their target organs and trigger the desired responses

hydrogen bonding: intermolecular force between the H of an N–H, O–H or F–H bond and a lone pair on O, N or F of an adjacent molecule

hydrolyze: to react with water

hydrophilic: having an affinity with water

hydrophobic: water repelling

hyperbolic relationship: a geometric system in which two or more lines can be drawn through any point in a plane and not intersect a given line in that plane

hyperpolarization: process of causing an increase in charge separation in nerve cells; opposite of depolarization

hypertension: condition in which blood pressure is abnormally high

Ibn Sina: given name of an Islamic scientist known in the West as Avicenna (979–1037); reputed to be the author of more than 100 books that were Europe's most important medical texts from the 12th century until the 16th century

inert: incapable of reacting with another substance

inhibitory: preventing an action that would normally occur

integro-differential: complex mathematical model used to calculate a phase transition

interface tension: contractile force at the junction of two liquids

intermediate: molecule, often short-lived, that occurs while a chemical reaction progresses but is not present when the reaction is complete

intermolecular force: force that arises between molecules, generally it is at least one order of magnitude weaker than the chemical bonding force

internuclear: distance between two nuclei

intestinal epithelium: layer of cells in the intestines that allows the passage of water and solutes

intramolecular force: force that arises within molecules—essentially the force associated with chemical bonds

invertebrate: category of animal that has no internal skeleton

in vitro: Latin, meaning "in glass" and applied to experiments done under artificial conditions, that is, in a test tube

in vivo: Latin, meaning "in life" and applied to experiments conducted in a living cell or organism

ion exchange chromatography: form of liquid-solid chromatography based on the reversible formation of bonds between the fixed ions bound to an insoluble matrix of an ion exchanger and mobile counter ions present in the liquid phase passing over the insoluble matrix

ionization: dissociation of a molecule into ions carrying + or − charges

isolate: part of a reaction mixture that is separated and contains the material of interest

isomer: molecules with identical compositions but different structural formulas

isoprene: common name for 2-methyl-1,3butadiene, the monomer of the natural rubber polymer

isostructural: relating to an arrangement of atomic constituents that is geometrically the same although different atoms are present

isotope: form of an atom that differs by the number of neutrons in the nucleus

ketone: one of the characteristic groups of atoms in organic compounds that undergoes characteristic reactions, generally irrespective of where it occurs in the molecule; the RC(O)R functional group

kinetic theory: theory of molecular motion

Kohlrausch drum: rotating cylinder used to mount a variable resistance slide wire for a polarograph

lanthanides: a family of elements (atomic number 57 through 70) from lanthanum to lutetium having from 1 to 14 4f electrons

lattice: systematic geometrical arrangement of atomic-sized units that describe the structure of a solid

ligand: molecule or ion capable of donating one or more electron pairs to a Lewis acid

lipid: a nonpolar organic molecule; fatlike; one of a large variety of nonpolar hydrophobic (water-hating) molecules that are insoluble in water

lipophilic: a molecule that tends to congregate in solution with lipids—it will be a nonpolar molecule or the nonpolar portion of a molecule

liposome: sac formed from one or more lipid layers that can be used for drug transport to cells in the body

liquefaction: process of changing to a liquid form

locomotor: able to move from place to place

Lucretius: Roman poet of first century B.C.E., also known as Titus Carus; author of *De Rerum Natura*

lysergic acid: one of the Ergot series of alkaloids, which constrict blood vessels so that the victim develops burning sensations in the limbs, gangrene, and, ultimately, convulsions; the diethylamide of this substance (LSD) induces visual perception disorders, delusion

lysis: breakdown of cells; also the favorable termination of a disease

macrolide: substance with a large ring lactone structure

macronutrient: one of a number of substances, needed in relatively large amounts, that provide nourishment for living organisms

macroscopic phenomena: events observed with human vision unassisted by instrumentation

mammalian toxicity: poisonous effect on humans and other mammals

Manhattan Project: government project dedicated to creation of an atomic weapon; directed by General Leslie Groves

manifold of ensemble states: a set of quantum states that meet the specific requirements (such as total energy) being considered in a calculation

mechanical energy: energy of an object due to its position or motion

mediate: to act as an intermediary agent

melting point: temperature at which a substance in the solid state undergoes a phase change to the liquid state

mentorship: the process by which a wise and trusted teacher guides a novice in the development of his/her abilities

metabolism: the complete range of biochemical processes that take place within living organisms; comprises processes that produce complex substances from simpler components, with a consequent use of energy (anabolism), and those that break down complex food molecules, thus liberating energy (catabolism)

metabolites: products of biological activity that are important in metabolism

metal: element or other substance the solid phase of which is characterized by high thermal and electrical conductivities

metal cation: positively charged ion resulting from the loss of one or more valence electrons

metalloenzyme: a protein enzyme that contains at least one metal atom, often in an active site of the protein

metalloid: elements that exhibit properties that are between those of metals and nonmetals; generally considered to include boron, silicon, germanium, arsensic, antimony, tellurium, and polonium

metallothionein: class of low molecular weight proteins and polypeptides with very high metal and sulfur content; thought to play a role in concentration and flow of essential elements, e.g., Cu and Zn, and in ameliorating the influence of toxic elements, e.g., Hg and Cd, in the body

metallurgy: the science and technology of metals

microchemistry: chemical investigation carried out on a microscopic level

microcrystalline: relating to the structure of crystals of very small size, typically a micron (μm) in dimension

micromolar: relating to a solution of a substance that is in the concentration range of micromoles per liter, or 10^{-6} moles per liter

mitochondrial matrix: soluble phase inside the inner mitochondrial membrane containing most of its enzymes

mitosis: process by which cells divide, particularly the division of the cell nucleus

molecular identity: "fingerprint" of a molecule describing the structure

monoclinic: one of several arrangements of atoms found in crystalline solids; characterized by a unit cell of three axes each of a differing length; two axes are mutually perpendicular while the third is at an oblique angle

monodentate: capable of donating one electron pair; literally, one-toothed

monosaccharide: one class of the natural products called carbohydrates with the general formula $C_x(H_2O)_y$; monosaccharides have a weak sweet taste, are readily soluble in water, and are called sugars

mordant dye: dye substance containing an acidic moiety, e.g., a carboxyl group, which binds metallic compounds, forming insoluble colored compounds

natural philosophy: study of nature and the physical universe

nesosilicate: any silicate in which the SiO_4 tetrahedra are not interlinked

net charge: total overall charge

neurologic: of or pertaining to the nervous system

neuropathy: degenerative state of the nerves or nervous system

neuropeptide: neurotransmitter released into the blood stream via nerve cells

neutron activation analysis: method for detecting traces of elements by bombardment with high-flux neutrons and then measuring the decay rate of the radioactive products

Newtonian: based on the physics of Isaac Newton

nicotine adenine dinucleotide (NAD): one compound of a group of coenzymes found in hydrogen-transferring enzymes

nitric oxide: compound, NO, which is involved in many biological processes; the drug Viagra enhances NO-stimulation of pathways to counteract impotence; may be involved in killing tumors

nitrotoluic acid: benzoic acid molecule with methyl and nitro groups attached

noble gas: element characterized by inert nature; located in the rightmost column in the Periodic Table

noncovalent: having a structure in which atoms are not held together by sharing pairs of electrons

noncovalent aggregation: non-specific interaction leading to the association of molecules

nonpolar: molecule, or portion of a molecule, that does not have a permanent, electric dipole

nuclear: (a) having to do with the nucleus of an atom; (b) having to do with the nucleus of a cell

nucleosynthesis: creation of heavier elements from lighter elements via fusion reactions in stars

octahedral: relating to a geometric arrangement of six ligands equally distributed around a Lewis acid; literally, eight faces

odd chain fatty acid: long chain carboxylic acid with an odd number of carbon atoms

oligomeric chain: chain that contains a few repeating units of a growing polymeric species

opioid: naturally produced opium-like substance found in the brain

optically active: capable of rotating the plane of plane-polarized light

organoleptic: effect of a substance on the five senses

organometallic compound: compound containing both a metal (transition) and one or more organic moieties

oxidation: process that involves the loss of electrons (or the addition of an oxygen atom)

oxidation state zero: condition characterized by an atom having neither lost nor gained electrons

oxidation–reduction reaction: reaction, sometimes called redox, that involves the movement of electrons between reactants to form products

oxide ion conductor: series of oxides of various compounds in perovskite structure—especially of interest in high-temperature fuel cells

parabolic curve: planar curve each point of which is equidistant from a straight line (axis)

paraffin: saturated aliphatic hydrocarbon (alkane), or hydrocarbon wax

partial pressure: portion of a total pressure of a gas mixture contributed by a single type of gas in the sample

passive diffusion: mechanism of transporting solutes across membranes

pasteurization: process of heating foods such as milk to destroy bacteria

peerage: a body of peers; dignitaries of equal standing

perpendicular: condition in which two lines (or linear entities like chemical bonds) intersect at a 90-degree angle

pH effect: effect caused by a change in the concentration of hydrogen ions

phase: homogenous state of matter

phenol: common name for hydroxybenzene (C_6H_5OH)

phosphorylation: the addition of phosphates into biological molecules

photodiode assembly: grouping of electronic devices which includes a photodiode—a photodetector; useful in medical diagnostics, bar code readers, and guidance systems

photon: a quantum of electromagnetic energy

photosynthesis: process by which plants convert carbon dioxide and water to glucose

physostigmine: alkaloid derived from the leaves of the Calabar bean, formula $C_{15}H_{12}N_3O_2$; salts used for anticholinesterase activity

pilot plant: intermediate stage of testing for chemical process, between bench-top and production scale

planar complex: arrangement of atoms in which all atoms lie within a common two-dimensional plane

plane polorized light: electromagnetic radiation (light) in which the electric (or magnetic) vectors are all vibrating in the same plane

platelet: smallest noncellular component of human blood

pneumatic chemist: early chemist who studied primarily the properties of gases

polynucleotide synthesis: formation of DNA or RNA

polypeptide: compound containing two or more amide units—C(O)NH—produced by the condensation of two or more amino acids

porphyrin: common type of heterocyclic ligand that has four five-member rings with a nitrogen, all of which lie in a plane; nitrogen atom lone pairs are available for coordinate covelent bonds

postsynaptic neuron: receptor nerve cell

potash: the compound potassium oxide, K_2O

precipitation: process of separating a solid substance out of a solution

precursor molecule: molecule that is the chosen starting point for the preparation of another molecule; a starting molecule in a chemical synthesis; a reactant molecule

primary electrochemical cell: voltaic cell based on an irreversible chemical reaction

principal oxidation state: oxidation state that is most important

prism: triangular-shaped material made from quartz or glass used to diffract light

prodrug: precursor of a drug that is converted into an active form by a metabolic process

progesterone: steroid found in the female reproductive system; formula $C_{21}H_{30}O_2$

prokaryotic: relating to very simple cells of the type found in bacteria

propagating: reproducing; disseminating; increasing; extending

protecting group: substance added to a functional group of a molecule preventing further reaction until the substance is removed by subsequent reactions

proximate percent: nearest percent of a population (e.g. people, substances)

purine base: one of two types of nitrogen bases found in nucleic acids

putative: commonly believed or hypothesized

pyramidal: relating to a geometric arrangement of four electron-donating groups at the four vertices of a pyramid

pyrimidine base: one of two types of nitrogen bases found in nucleic acids

pyruvate: anion of pyruvic acid produced by the reaction of oxygen with lactic acid after strenuous exercise

quantum: smallest amount of a physical quantity that can exist independently, especially a discrete amount of electromagnetic energy

quantum mechanical: theoretical model to describe atoms and molecules by wave functions

quantum physics: physics based on the fact that the energy of an electron is equal to its frequency times Planck's constant

radioactive decay: process involving emission of subatomic particles from a nucleus, typically accompanied by emission of very short wavelength electromagnetic radiation

radioelement: a radioactive element; one in which the nucleus spontaneously decomposes (decays) producing α (alpha) and β (beta) particles and γ (gamma) rays

rare earth elements: older name for the lanthanide series of elements, from lanthanum to lutetium

rate-limiting step: slowest step in a complex reaction; it determines the rate of the overall reaction; sometimes called the rate-determining step

reagent: chemical used to cause a specific chemical reaction

receptor: area on or near a cell wall that accepts another molecule to allow a change in the cell

reducing agent: substance that causes reduction, a process during which electrons are lost (or hydrogen atoms gained)

reducing potential: stored energy capable of making a chemical reduction occur

relativistic calculation: quantum mechanical model that includes the effects of relativity, particularly for core electrons

repulsive force: force that repels two bodies; charges of the same sign repel each other

reserpine: one of a group of alkaloids found naturally in the shrub *Rarewolfia serpentina*; has been used for centuries to treat hypertension, insomnia, and mental disorders; more recently it has been used to reduce blood pressure

retardation: to slow down a chemical reaction

retrosynthetic analysis: method of analyzing chemical reactions that starts with the product and works backward to determine the initial reactants

reverberator furnace: furnace or kiln used in smelting that heats material indirectly by deflecting a nearby flame downward from the roof

ribosome: large complex of proteins used to convert amino acids into proteins

RNA: ribonucleic acid, a natural polymer used to translate genetic information in the nucleus into a template for the construction of proteins

RNA polymerase: enzyme used to make RNA using DNA as a template

rough endoplasmic reticulum: regions of endoplasmic reticulum the outer surfaces of which are heavily studded with ribosomes, which make proteins for activities within membrane-bounded organelles

Royal Society: The U.K. National Academy of Science, founded in 1660

rutile: common name of TiO_2; also a common structural type for compounds with the general composition AB_2

saltpeter: potassium nitrate; chile saltpeter is sodium nitrate

screen: process of comparing multiple reagents simultaneously to provide information on reaction of one reagent with another

seed germination: beginning of the process by which a seed produces a new plant

selenium toxicity: condition created by intake of excess selenium (Se) from plants or seleniferous water; acute and chronic toxicity are known

semisynthetic: produced by synthesis from natural starting materials

serology: the study of serum and reactions taking place within it

sigma plus pi bonding: formation of a double bond within a molecule or ion

single Slater determinant: wave function used to describe atoms and molecules

size of the basis set: number of relatively simple mathematical functions (called the basis set) used to represent a more complicated mathematical function such as an atomic orbital

smelting: process by which ores are reduced in the production of metals

Socrates: Greek philosopher, c.470–399 B.C.E.

somatic cell: cells of the body with the exception of germ cells

spectral line: line in a spectrum representing radiation of a single wavelength

spectroscopy: use of electromagnetic radiation to analyze the chemical composition of materials

spinel: name given to a group of minerals that are double oxides of divalent and trivalent metals, for example, $MgO \cdot Al_2O_3$ or $MgAl_2O_4$; this mineral is called spinel; also a structural type

stacking interactions: one type of interaction that affects conformation of double-stranded DNA; caused by van der Waals forces

stereospecific: yielding one product when reacted with a given compound but the opposite product when reacted with its stereoisomer

steric repulsion: repulsive force that exists when two atoms or groups get too close together

sterol: steroid containing an alcohol group; derived from plants or animals; e.g., cholesterol

stigmasterol: sterol found in soybeans, $C_{29}H_{48}O$

stratosphere: layer of the atmosphere where ozone is found; starts about 6.2 mi (10 km) above ground

streptomycin: antibiotic produced by soil bacteria of genus *Streptomyces*

subcritical: mass of nuclear materials below the amount necessary to cause a chain reaction

subshell: electron energy sublevel, of which there are four: *s*, *p*, *d*, and *f*

sulfonamides: first of a series of drugs used for the prevention and cure of bacterial infections in humans; sulfanomides are amides of sulfuric acids and contain the $–SO_2NRR_1$ group

super-heavy elements: elements of atomic number greater than 103

superhelix: helical-shaped molecule synthesized by another helical-shaped molecule

surfactants: surface-active agents that lower the surface tension of water; e.g., detergents, wetting agents

synaptic cleft: tiny space between the terminal button of one neuron and the dendrite or soma of another

synthesis: combination of starting materials to form a desired product

synthon: in retrosynthesis, molecules are broken into characteristic sections called synthons

tetrachloride: term that implies a molecule has four chlorine atoms present

tetravalent oxidation state: bonding state of an atom that can form four bonds

theoretical physics: branch of physics dealing with the theories and concepts of matter, especially at the atomic and subatomic levels

3′ end: situation in nucleic acids in which the phosphate group is attached at the third carbon atom from where the base is attached

thykaloid membrane: part of a plant that absorbs light and passes the energy on to where it is needed

thymine: one of the four bases that make up a DNA molecule

toluic acids: methylbenzoic acids

torsion balance: instrument used to measure small forces (weights), based upon the resistance of a wire to be twisted

toxicology: division of pharmacology dealing with poisons, their identification, detection, effects on the body, and remedies

toxin: poisonous substance produced during bacterial growth

trace element: element occurring only in a minute amount

transcription: enzyme-catalyzed assembly of an RNA molecule complementary to a strand of DNA

transition metal complex: species formed when a transition metal reacts with ions or molecules, including water

transition metals: elements with valence electrons in d-sublevels; frequently characterized as metals having the ability to form more than one cation

translational process: transfer of information from codon on mRNA to anticodon on tRNA; used in protein synthesis

trigonal bipyramidal: geometric arrangement of five ligands around a central Lewis acid, with ligands occupying the vertices of two trigonal pyramids that share a common face; three ligands share an equatorial plane with the central atom, two ligands occupy an axial position

tropocollagen: fibers, or fibrils, consisting of three polypeptide sequences arranged in a helix

tyrosine: one of the common amino acids

ultraviolet radiation: portion of the electromagnetic spectrum with wavelengths shorter than visible but longer than x rays

uracil: heterocyclic, pyrimidine, amine base found in RNA

valence: combining capacity

vertabrates: animals that have a skeleton

vesicle: small compartment in a cell that contains a minimum of one lipid bilayer

vitamins: organic molecules needed in small amounts for the normal function of the body; often used as part of an enzyme catalyzed reaction

vitriol: sulfate of a metal; there are blue (Cu), white (Zn), green (Fe), and rose (Co) vitriols

volatile: low boiling, readily vaporized

voltage: potential difference expressed in volts

vulcanized rubber: chemical process of mixing rubber with other materials like sulfur; it strengthens rubber so it can be used under hot or cold conditions; discovered by Charles Goodyear

wetting agent: molecule that, when added to a liquid, facillitates the spread of the liquid across a surface

zoology: branch of biology concerned with the animal kingdom

zwitterion: molecule that simultaneously contains a positive and a negative charge