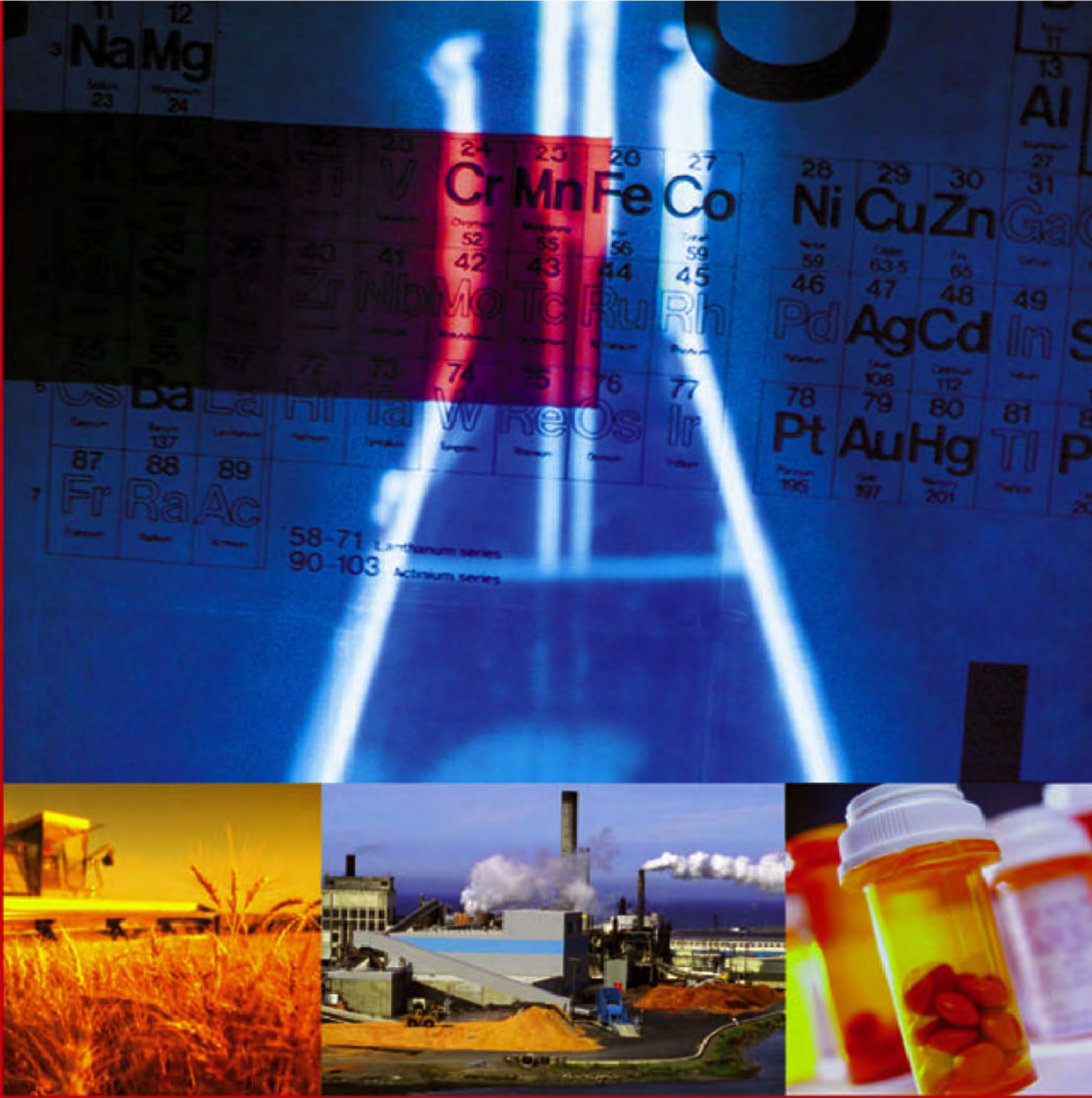

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Chemistry: Foundations and Applications
J. J. Lagowski, Editor in Chief

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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

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Astrochemistry

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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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A, Vitamin *See* ***Retinol***.

a

Acetaminophen

The drug acetaminophen is a pain reliever (an **analgesic**) and a fever-**reducing agent** (an antipyretic). It is found in over-the-counter medicines such as Tylenol and Excedrin. It is widely used to treat both chronic and acute pain and is considered to have a pain-relieving potency similar to that of other over-the-counter analgesics, such as aspirin and ibuprofen. Its chemical name is 4-hydroxyacetanalide. Its chemical formula is $C_8H_9NO_2$ (see Figure 1).

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

reducing agent: substance that causes reduction, a process during which electrons are lost (or hydrogen atoms gained)

Acetaminophen was used as a pain reliever as early as the late 1800s. It was approved for use by the U.S. Food and Drug Administration in 1950, shortly after it was discovered that the closely related drug paracetin was broken down in the body to acetaminophen, and that the beneficial effects of paracetin were actually the effects of acetaminophen.

Acetaminophen works by inhibiting the **synthesis** of chemical messengers called prostaglandins, which help to transmit pain signals and induce fever. The body produces prostaglandins in response to an injury or illness. Acetaminophen reduces the pain by helping to block this signaling. Acetaminophen stops some prostaglandin functions while not affecting others. Prostaglandins are known to promote inflammation and swelling of many body tissues. Unlike aspirin and ibuprofen, acetaminophen does not have anti-inflammatory action.

synthesis: combination of starting materials to form a unified product

The differences in the actions of these drugs involve their tissue specificities. Aspirin and ibuprofen act on a broad range of tissues. Acetaminophen inhibits prostaglandin synthesis more specifically in the cells of the nervous system and is a much less effective inhibitor of this in other tissues. This selectivity gives acetaminophen its analgesic and antipyretic effects without acetaminophen's acting as an anti-inflammatory drug.

Acetaminophen is known to cause less stomach irritation than aspirin and ibuprofen, and it does not inhibit **platelet** aggregation and blood clotting (as does aspirin).

platelet: smallest noncellular component of human blood

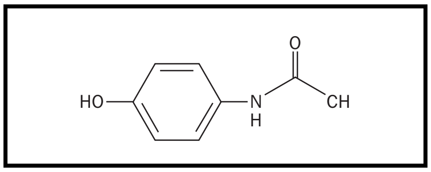

Figure 1. Structure of acetaminophen.

When given in its therapeutic dose (500 mg every 4–6 hours), acetaminophen is a safe and effective pain reliever. However, at higher doses it can be severely toxic to the liver, and even fatal.

excrete: to eliminate or discharge from a living entity

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)

The drug itself is not toxic, but a toxic compound, N-acetyl-*p*-benzoquinonimine, is formed from it as it is broken down by enzymes in the liver. In small amounts this compound can be detoxified and **excreted**. But in large amounts it overwhelms the detoxification system and the compound begins killing liver tissue. Overdose can be treated by giving the patient activated charcoal, which absorbs the acetaminophen in the patient's stomach and intestines, and by administering *N*-acetylcystine, a compound that can deactivate the toxic product of **metabolism**. SEE ALSO ACETYLSALICYLIC ACID; IBUPROFEN.

Kyle Knight

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Acetylcholine

Acetylcholine is the neurotransmitter produced by neurons referred to as cholinergic neurons. In the peripheral nervous system acetylcholine plays a role in skeletal muscle movement, as well as in the regulation of smooth muscle and cardiac muscle. In the central nervous system acetylcholine is believed to be involved in learning, memory, and mood.

vesicle: small compartment in a cell that contains a minimum of one lipid bilayer

synaptic cleft: tiny space between the terminal button of one neuron and the dendrite or soma of another

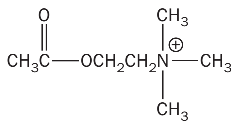
receptor: area on or near a cell wall that accepts another molecule to allow a change in the cell

Acetylcholine is synthesized from choline and acetyl coenzyme A through the action of the enzyme choline acetyltransferase and becomes packaged into membrane-bound **vesicles**. After the arrival of a nerve signal at the termination of an axon, the vesicles fuse with the cell membrane, causing the release of acetylcholine into the **synaptic cleft**. For the nerve signal to continue, acetylcholine must diffuse to another nearby neuron or muscle cell, where it will bind and activate a **receptor** protein.

depolarization: process of decreasing the separation of charge in nerve cells; the opposite of hyperpolarization

There are two main types of cholinergic receptors, nicotinic and muscarinic. Nicotinic receptors are located at synapses between two neurons and at synapses between neurons and skeletal muscle cells. Upon activation a nicotinic receptor acts as a channel for the movement of ions into and out of the neuron, directly resulting in **depolarization** of the neuron. Muscarinic receptors, located at the synapses of nerves with smooth or cardiac muscle, trigger a chain of chemical events referred to as signal transduction.

For a cholinergic neuron to receive another impulse, acetylcholine must be released from the receptor to which it has bound. This will only happen if the concentration of acetylcholine in the synaptic cleft is very low. Low synaptic concentrations of acetylcholine can be maintained via a hydrolysis reaction catalyzed by the enzyme acetylcholinesterase. This enzyme hydrolyzes acetylcholine into acetic acid and choline. If acetylcholinesterase activity is inhibited, the synaptic concentration of acetylcholine will remain higher than normal. If this inhibition is irreversible, as in the case of exposure to many nerve gases and some pesticides, sweating, bronchial constriction, convulsions, paralysis, and possibly death can occur. Although irreversible inhibition is dangerous, beneficial effects may be derived from transient (reversible) inhibition. Drugs that inhibit acetylcholinesterase in a



$$CH_3\overset{\overset{O}{\|}}{C}-OCH_2CH_2\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{N^{\oplus}}}-CH_3$$

Figure 1. The structure of acetylcholine.

reversible manner have been shown to improve memory in some people with Alzheimer's disease. SEE ALSO NEUROTRANSMITTERS.

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Acetylsalicylic Acid

Aspirin (acetylsalicylic acid, see Figure 1) was introduced as an **analgesic** (pain-relieving agent) in the late nineteenth century by chemists at Bayer, a German pharmaceutical company. Acetylsalicylic acid is a **prodrug** and is transformed in the body to salicylate, the active form of the drug. Salicylates are also anti-inflammatory (i.e., prevent swelling and phenomena related to swelling associated with trauma or allergic response). Salicylates were initially isolated from white willow (*Salix alba*) bark, from which the name of the drug is derived. Indeed, ancient Greek physicians, notably **Hippocrates** and Dioscorides, suggested chewing on willow bark to relieve pain.

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

prodrug: compound that is converted to its active form after being administered or ingested

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

Although aspirin is chiefly extolled for its analgesic properties, it has other equally important therapeutic benefits. Aspirin is an antipyretic (fever-reducing) agent and is used to reduce elevated body temperature. Since the 1980s aspirin has been prescribed for the prevention of heart attack and stroke. Recent studies suggest that aspirin may guard against colon cancer.

Acetylsalicylic acid is a weak acid ($pK_a = 3.5$) that can be absorbed across the mucosal lining of the stomach. However, most of the drug is absorbed from the upper regions of the small intestine. Once the drug has entered the bloodstream it is hydrolyzed to acetic acid and salicylic acid (see Figure 2).

The most widely recognized mode of action of the salicylates is the inhibition of the formation of prostaglandins. Prostaglandins are 20-carbon molecules having side chains of varying degrees of saturation and **oxidation**, synthesized from polyunsaturated fatty acids in the body in response to tissue damage. The localized release of prostaglandins in response to injury or invasion by foreign agents (antigens) results in an increased blood flow to the affected area, and stimulation of the sensory nerve endings that **mediate** pain. Salicylates inhibit prostaglandin **synthesis** by binding to prostaglandin cyclooxygenases (the enzymes responsible for transforming fatty acids into prostaglandins), thereby inactivating the enzymes.

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

mediate: to act as an intermediary agent

synthesis: combination of starting materials to form a desired product

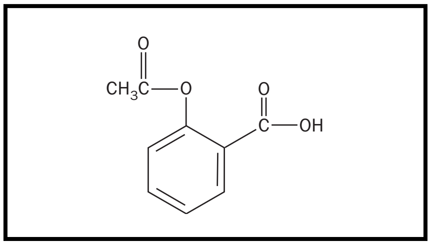
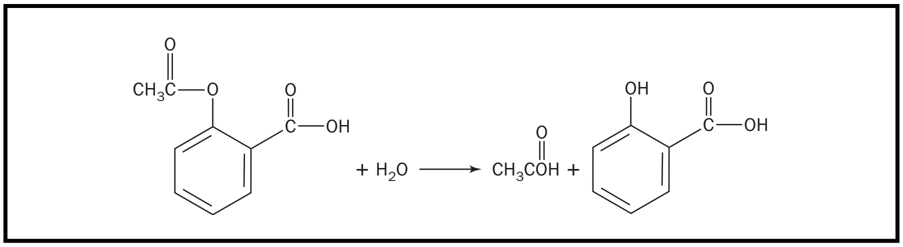


Figure 1. Structure of acetylsalicylic acid.

Aspirin is one of the most widely used drugs in modern society. It is most frequently used to treat mild to moderate pain or to reduce fever. Because of its anti-inflammatory action, aspirin is prescribed to individuals who suffer from joint inflammation conditions such as rheumatoid arthritis and osteoarthritis. In addition to its antipyretic, anti-inflammatory, and analgesic properties, aspirin is also prescribed to patients at high risk for heart attack

Figure 2. Hydrolysis of acetylsalicylic acid to acetic acid and salicylic acid.



retardation: to slow down a chemical reaction

platelet: smallest noncellular component of human blood

or stroke. Salicylates **retard** the clotting of blood by inhibiting **platelet** aggregation. When platelets aggregate, clotting is promoted and blood flow through vessels and valves is impeded. A stroke results when blood flow to regions of the brain is blocked. Aspirin inhibits enzymes in platelet membranes responsible for the formation of platelet aggregation factors, and thus reduces the risk of blood clots. Enzyme inhibition may also be responsible for aspirin's purported anticancer action. Recent findings suggest that regular doses of aspirin reduce the risks of some cancers (particularly colon cancer). Although scientists do not know how aspirin reduces the risk of cancer, they suspect it could be related to its anti-inflammatory effects and its ability to inhibit enzymes produced by some cancer cells.

FRIEDRICH BAYER (1825–1880)

In 1863 Friedrich Bayer cofounded a dye manufacturing company in Germany. Eight years after his death, in 1888 the company opened a pharmaceutical division. A decade later, employee Felix Hoffman, concerned over his father's aches and pains, discovered a useful chemical in the waste of the dye process. Known as aspirin, it remains a popular painkiller over 100 years later.

—Valerie Borek

Not all of aspirin's health effects are beneficial. Salicylate therapy is associated with many adverse side effects, generally pertaining to the gastrointestinal system. Gastric ulcers and gastric bleeding can occur in individuals on high doses of aspirin. More worrisome is the occurrence of Reye's syndrome in children with viral illnesses such as influenza or chicken pox who have been given aspirin. Reye's syndrome is a serious condition characterized by sudden vomiting, violent headaches, and, in 20 to 30 percent of cases, death. Because of the potential risk of Reye's syndrome in young people administered aspirin, many physicians and the Food and Drug Administration (FDA) warn against the use of salicylates in children under sixteen years of age. SEE ALSO Acetaminophen; Acid-Base Chemistry; Hydrolysis; Ibuprofen.

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Acid-Base Chemistry

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

Acids and bases have been known by their properties since the early days of experimental chemistry. The word "acid" comes from the Latin *acidus*, meaning "sour" or "tart," since water solutions of acids have a sour or tart taste. Lemons, grapefruit, and limes taste sour because they contain citric acid and ascorbic acid (**vitamin** C). Another common acid is vinegar, which is the sour liquid produced when apple cider, grape juice, or other plant juices ferment beyond the formation of alcohol. Vinegar is a 5 percent water solution of acetic acid. Besides having a sour taste, acids react with active **metals** to give hydrogen, they change the colors of indicators (for example, litmus turns from blue to red), and they neutralize bases. Bases change the colors of indicators (litmus turns from red to blue) and they neutralize acids. Hence, bases are considered the chemical opposite of acids.

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

Most common acid-base reactions take place in water solutions (commonly referred to as **aqueous solutions**). One of the earliest definitions of acids, advanced by the Swedish physicist and chemist Svante Arrhenius in 1887, stated that acid ionizes in aqueous solution to produce hydrogen ions (which are protons), H^+, and **anions**; and a base ionizes in aqueous solution to produce hydroxide ions (OH^-) and cations. Later studies of aqueous solutions provided evidence of a small, positively charged hydrogen ion combining with a water molecule to form a hydrated proton, $H^+(H_2O)$ or H_3O^+, which is called the hydronium ion. Often, the hydronium ion or hydrated proton is represented as H^+ (*aq*). Hydrogen chloride (HCl), a gas, is an acid because it dissolves in water to yield hydrogen ions and chloride ions. This water solution of HCl is referred to as hydrochloric acid.

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

anion: negatively charged chemical unit, like Cl^-, CO_{32}^-, or NO_3^-

$$HCl\ (g) \xrightarrow{H_2O} H^+\ (aq) + Cl^-\ (aq) \qquad (1)$$

A typical base, according to the Arrhenius definition, is sodium hydroxide (NaOH). It dissolves in water to give sodium ions and hydroxide ions.

$$NaOH\ (s) \xrightarrow{H_2O} Na^+\ (aq) + OH^-\ (aq) \qquad (2)$$

Neutralization

In the reaction of an acid with a base in aqueous solution, the hydrogen ions of the acid react with the hydroxide ions of the base to give water. The second product is a salt, which is composed of the positive metal ion from the base and the negative ion from the acid. For example,

$$HCl\ (aq) + KOH\ (aq) \rightarrow H_2O\ (l) + KCl\ (aq) \qquad (3)$$

Since HCl (*aq*) and KOH (*aq*) are fully ionized in solution, the preceding equation can be written as

$$H^+\ (aq) + Cl^-\ (aq) + K^+\ (aq) + OH^-\ (aq) \rightarrow$$
$$H_2O\ (l) + K^+\ (aq) + Cl^-\ (aq) \qquad (4)$$

Ions common to both sides can be canceled to yield

$$H^+\ (aq) + OH^-\ (aq) \rightarrow H_2O\ (l) \qquad (5)$$

This is referred to as the net ionic equation for the neutralization reaction. If H_3O^+ is substituted for H^+ (*aq*), the neutralization equation becomes

$$H_3O^+\ (aq) + OH^-\ (aq) \rightarrow 2\ H_2O\ (l) \qquad (6)$$

Strengths of Acids and Bases

The strength of an acid or base is determined by the extent of its **ionization** in aqueous solution. Strong acids, such as hydrochloric acid, are 100 percent ionized in aqueous solution, whereas weak acids, such as acetic acid, are less than 5 percent ionized. Experimentally, the extent of ionization is determined by measuring the electrical conductance of solutions. Strong acids and bases are strong electrolytes, and weak acids and bases are weak

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

Table 1. Common acids and bases.

COMMON ACIDS AND BASES

Strong Acids		**Strong Bases**	
HCl	hydrochloric acid	NaOH	sodium hydroxide
HNO_3	nitric acid	KOH	potassium hydroxide
H_2SO_4	sulfuric acid	$Ba(OH)_2$	barium hydroxide
Weak Acids		**Weak Bases**	
CH_3COOH	acetic acid	NH_3	ammonia
H_2CO_3	carbonic acid	CH_2NH_2	methyl amine
H_3PO_4	phosphoric acid		

electrolytes. Table 1 lists some common acids and bases and indicates whether they are strong or weak.

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

For weak acids and bases, partial ionization is a dynamic **equilibrium** between unionized molecules and its ion, as indicated by the double arrow in equation (7). For example, acetic acid is only partially ionized in aqueous solution

$$CH_3COOH\ (aq) \rightleftarrows H^+\ (aq) + CH_3COO^-\ (aq) \qquad (7)$$

In acetic acid, hydrogen ions and acetate ions recombine to form acetic acid molecules. The double arrow signifies that at any given instant, less than 5 percent of acetic acid molecules dissociate into hydrogen ions and acetate ions, while the hydrogen ions and acetate ions recombine to form acetic acid molecules.

Ammonia (NH_3) is a weak base, and although it does not have OH^- ions in its formula, it produces the ion on reaction with water.

$$NH_3\ (aq) + H_2O\ (l) \rightleftarrows NH_4^+\ (aq) + OH^-\ (aq) \qquad (8)$$

Brønsted-Lowry Theory

A major problem with Arrhenius's acid-base theory is that some substances, like ammonia, produce basic solutions and react with acids, but do not contain hydroxide ions. In 1923 Johannes Brønsted, a Danish chemist, and Thomas Lowry, an English chemist, independently proposed a new way to define acids and bases. An acid donates hydrogen ions (also called a proton donor); a base accepts hydrogen ions (also called a proton acceptor). These definitions not only explain all the acids and bases covered by Arrhenius's theory, they also explain the basicity of ammonia and ions such as carbonate, CO_3^{2-}, and phosphate, PO_4^3.

The Brønsted-Lowry theory includes water as a reactant and considers its acidity or basicity in the reaction. In the partial ionization of acetic acid, water is a base because it accepts the hydrogen ion to form hydronium ion.

$$\underset{\text{acid}}{CH_3COOH\ (aq)} + \underset{\text{base}}{H_2O\ (l)} \rightleftarrows \underset{\text{conjugate acid}}{H_3O^+\ (aq)} + \underset{\text{conjugate base}}{CH_3COO^-\ (aq)} \qquad (9)$$

In the reaction, a new acid and a new base are formed, which are called the conjugate acid and conjugate base, respectively. The hydronium ion, H_3O^+, is the conjugate acid of the base, H_2O, and the acetate ion, CH_3COO^-, is

THOMAS M. LOWRY (1874–1936)

A meticulous experimenter, Thomas Lowry is best known for his conceptualization of acid–base chemistry. Studies of nitrogenous compounds led Lowry to question fundamental aspects of the role of hydrogen during acid–base reactions. Three months before Brønsted published his theory, Lowry released his own similar thoughts on proton acceptors and donors in print.

—Valerie Borek

CONJUGATE ACID-BASE PAIRS

	Acid	Conjugate Base	
Strong acids	H_2SO_4	HSO_4^-	Weak bases
	HCl	Cl^-	
	H_3O^+	H_2O	
	HSO_4^-	$SO_4^{\ -}$	
	H_3PO_4	$H_2PO_4^-$	
	CH_3COOH	CH_3COO^-	
	H_2CO_3	HCO_3^-	
	$H_2PO_4^-$	HPO_4^{2-}	
	NH_4^+	NH_3	
	HCO_3^-	CO_3^{2-}	
	HPO_4^{2-}	PO_4^{3-}	
Weak acids	H_2O	OH^-	Strong bases

Table 2. Conjugate acid-base pairs.

the conjugate base of acetic acid, CH_3COOH. A pair of molecules or ions related to one another by the gain or loss of a single hydrogen ion is called a conjugate acid-base pair. In the reaction of ammonia, water is an acid because it donates a hydrogen ion to ammonia.

$$\underset{\text{base}}{NH_3\ (aq)} + \underset{\text{acid}}{H_2O\ (l)} \rightleftarrows \underset{\text{conjugate acid}}{NH_4^+\ (aq)} + \underset{\text{conjugate base}}{OH^-\ (aq)} \tag{10}$$

This ability of water to donate or accept hydrogen ions, depending on whether it reacts with a base or an acid, is referred to as "amphiprotic." The conjugate acid-base pairs in this reaction are NH_3/NH_4^+ and H_2O/OH^-.

The Brønsted-Lowry definitions also explain why carbonate salts such as sodium carbonate (washing soda) dissolve in water to give basic solutions. Carbonate ion removes a hydrogen ion from a water molecule, which leaves behind a hydroxide ion:

$$\underset{\text{base}}{CO_3^{2-}\ (aq)} + \underset{\text{acid}}{H_2O\ (l)} \rightleftarrows \underset{\text{conjugate acid}}{HCO_3^-\ (aq)} + \underset{\text{conjugate base}}{OH^-\ (aq)} \tag{11}$$

In the preceding reaction, water and hydroxide ion are a conjugate acid-base pair, whereas carbonate ion and bicarbonate ion are a conjugate base-acid pair. Every Brønsted-Lowry acid has a conjugate base, and every Brønsted-Lowry base has a conjugate acid. Familiarity with conjugate acid-base pairs is important to understanding the relative strengths of acids and bases. Table 2 lists some conjugate acid-base pairs and their relative strengths. Strong acids have weak conjugate bases, and weak acids have strong conjugate bases.

Polyprotic Acids

Several common acids have more than one ionizable hydrogen ion (Table 1). Each successive hydrogen ion in these polyprotic acids ionizes less readily. For example, sulfuric acid is a strong acid because of the complete ionization of the first hydrogen ion.

$$H_2SO_4\ (aq) + H_2O\ (l) \rightarrow H_3O^+\ (aq) + HSO_4^-\ (aq) \tag{12}$$

The HSO_4^- also acts as an acid, but it is not 100 percent ionized, so HSO_4^- is an acid of moderate strength. For example, sodium hydrogen sulfate is used to increase the acidity of swimming pools, whereas sodium carbonate is used to increase the basicity of swimming pools.

$$HSO_4^- (aq) + H_2O (l) \rightleftarrows H_3O^+ (aq) + SO_4^{2-} (aq) \qquad (13)$$

Phosphoric acid has three ionizable hydrogen ions. Each stepwise ionization of phosphoric acid occurs to a lesser extent than the one before it. Phosphoric acid is stronger than acetic acid because the first step ionizes to a greater extent than acetic acid.

$$H_3PO_4 (aq) + H_2O (l) \rightleftarrows H_3O^+ (aq) + H_2PO_4^- (aq) \qquad (14)$$

However, $H_2PO_4^-$ is a weaker acid than acetic acid because the second ionization is much smaller (by a factor of 10^5) than the first step.

$$H_2PO_4^- (aq) + H_2O (l) \rightleftarrows H_3O^+ (aq) + HPO_4^{2-} (aq) \qquad (15)$$

The third ionization is also much smaller than the second step (by a factor of 10^5).

$$HPO_4^{2-} (aq) + H_2O (l) \rightleftarrows H_3O^+ (aq) + PO_4^{3-} (aq) \qquad (16)$$

The anions of phosphoric acid can also accept hydrogen ions and act as bases with a strong acid like hydrochloric acid. For example,

$$PO_4^{3-} (aq) + H_3O^+ (aq) \rightleftarrows HPO_4^{2-} (aq) + H_2O (l) \qquad (17)$$

Ions such as $H_2PO_4^-$, HPO_4^{2-}, HCO_3^-, and HSO_4^- can act as an acid by donating a hydrogen ion or as a base by accepting a hydrogen ion. This ability to act as either an acid or a base is referred to as an amphoteric property.

The pH Scale

The Brønsted-Lowry acid-base definitions are based on the amphiprotic properties of water: Water is capable of acting as both a hydrogen ion donor and a hydrogen ion acceptor, depending on the acidic or basic properties of the dissolved substance (equations 9 and 10). Water can also act as a proton donor and proton acceptor towards itself. This is referred to as the autoionization of water.

$$H_2O (l) + H_2O (l) \rightleftarrows H_3O^+ (aq) + OH^- (aq) \qquad (18)$$

Pure water is neutral because it contains equal numbers of hydronium ions and hydroxide ions. However, pure water only slightly ionizes, about 1 in every 55,000,000 water molecules is ionized at any given time. The actual molar concentration of hydronium ions and hydroxide ions in pure water at 25°C is 1.0×10^{-7}. The product of the molarity of the hydronium ions and hydroxide ions of pure water is $(1.0 \times 10^{-7})(1.0 \times 10^{-7}) = 1.0 \times 10^{-14}$.

The value of 1.0×10^{-14} is important to the study of aqueous solutions of acids and bases because it is a constant that is always the product of the molar concentration of H_3O^+ and OH^-.

$$[H_3O^+] [OH^-] = 1.0 \times 10^{-14} \qquad (19)$$

If acid is added to pure water, the concentration of H_3O^+ will be greater than 1.0×10^{-7}, and then the concentration of OH^- will be less than 1.0×10^{-7}. However, the product of the two must equal 1.0×10^{-14}. This relationship is the basis for calculating the concentration of one of the two ions, hydronium or hydroxide, when the other one is known. For example, a 0.1 M solution of hydrochloric acid is 0.1 M in H_3O^+ since hydrochlo-

pH OF COMMON SUBSTANCES

pH	$[H_3O^+]$, M	Example
0	1.0	Battery acid, 1 M sulfuric acid
1	0.1	Stomach acid, 0.1 M hydrochloric acid
2	1×10^{-2}	Lemon juice
3	1×10^{-3}	Vinegar
4	1×10^{-4}	Soft drink
5	1×10^{-5}	Rain water
6	1×10^{-6}	Milk
7	1×10^{-7}	Pure water
8	1×10^{-8}	Baking soda, $NaHCO_3$
9	1×10^{-9}	Washing soda, Na_2CO_3
10	1×10^{-10}	Milk of magnesia, $Mg(OH)_2$
11	1×10^{-11}	Aqueous household ammonia, NH_3
12	1×10^{-12}	Limewater, $Ca(OH)_2$
13	1×10^{-13}	Drano, 0.1 M NaOH
14	1×10^{-14}	Drano, 1.0 M NaOH

Table 3. pH of common substances.

ric acid is fully ionized. From the equation, the molar concentration of OH^- is 10^{-13}. For a 0.1 *M* solution of NaOH, the OH^- is 0.1 *M*, but the hydrogen ion concentration is 10^{-13}. Hence, the value of the exponent for hydronium ion concentration goes from -1 in strong 0.1 *M* acid to -13 in strong 0.1 *M* base.

In 1909 the Danish biochemist S. P. L. Sørensen proposed that these exponents be used as a measure of acidity. He devised a scale that would be useful in testing the acidity of Danish beer. Sorensen's scale came to be known as the pH scale, from the French *pouvoir hydrogene*, which means hydrogen power. pH is defined as the negative logarithm (log) of the hydronium ion concentration.

$$pH = -\log[H_3O^+] \tag{20}$$

The brackets around hydronium ion mean moles per liter of hydronium ions.

The pH scale includes values between 0 and 14. The pH of pure water is 7 because $[H_3O^+]$ is 1.0×10^{-7}. The pH of 0.1 *M* HCl is 1$[-\log 10^{-1} = -(-1)]$. The pH of 0.1 *M* NaOH is 13$(-\log 10^{-13}) = 13$. The pH scale does not apply to concentrations greater than 1.0 *M* for a strong acid ($pH = 0$) or 1.0 *M* for a strong base ($pH = 14$).

For solutions in which $[H_3O^+]$ is not an exact power of 10 (0.1, 0.01, . . .), a calculator can be used to determine the logarithm. For example, if the $[H_3O^+]$ is 1.5×10^{-3} *M*, the logarithm is $-3 + \log 1.5 = -3 + 0.18 = -2.82$, and the pH is $-(-2.82)$ or 2.82. Table 3 provides the pH values of some common solutions.

Acid-Base Indicators

Many natural substances are acid-base indicators. The most familiar one is litmus, an organic dye extracted from certain lichens. Litmus turns from blue to red in acidic solutions ($<$ pH 7) and from red to blue in basic solutions ($\sim$ pH 7). Some other natural indicators include red cabbage extract, blueberry juice, black tea, beet juice, rhubarb, and tomato leaves, and flowers such as the rose, daylily, blue iris, and purple dahlia. Red cabbage extract undergoes sharp changes of color at several pH values. The deep purple color of red cabbage leaves is caused by a mixture of water-soluble

Table 4. Common acid-base indicators.

COMMON INDICATORS

Indicator	pH Range	Color Change
Thymol blue	1.2 – 2.8	red → yellow
Methyl red	4.4 – 6.2	red → yellow
Litmus	5 – 8	red → blue
Bromothymol blue	6.2 – 7.6	yellow → blue
Phenolphthalein	8.0 – 10.0	colorless → pink

anthocyanins. Over the pH range of 2 to 12, these anthocyanins change from red (pH 2) to pink (pH 4) to purple (pH 6–7) to green (pH 10) to yellow (pH 12), which makes red cabbage extract a "universal indicator."

Acid-base indicators are weak acids and bases. A typical indicator will ionize in aqueous solution according to the equation

$$\mathrm{HIn}\ (aq) + \mathrm{H_2O}\ (l) \rightleftarrows \mathrm{H_3O^+}\ (aq) + \mathrm{In^-}\ (aq) \qquad (21)$$

The chemical species HIn and In^- are different colors. When the solution is acidic to the degree that the HIn species dominates, it will be the color of HIn. When the solution is more basic with In^- dominating, it will be the color of In^-. Some common indicators and the pH ranges for their color changes are listed in Table 4.

Buffer Solutions

Buffer solutions contain a base and an acid that can react with an added acid or base, respectively, and they maintain a pH very close to the original value. Buffers usually consist of approximately equal quantities of a weak acid and its conjugate base, or a weak base and its conjugate acid. For example, a buffer solution of acetic acid and its conjugate base, the acetate ion, can neutralize small amounts of a strong acid or strong base as follows:

$$\mathrm{CH_3COOH}\ (aq) + \mathrm{OH^-}\ (aq) \rightarrow \mathrm{CH_3COO^-}\ (aq) + \mathrm{H_2O}\ (l) \qquad (22)$$

$$\mathrm{CH_3COO^-}\ (aq) + \mathrm{H_3O^+}\ (aq) \rightarrow \mathrm{CH_3COOH}\ (aq) + \mathrm{H_2O}\ (l) \qquad (23)$$

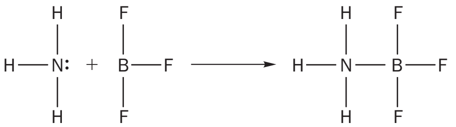
As illustrated in equations (22) and (23), the addition of either a strong base or a strong acid produces one of the components of the buffer mixture and so the pH does not change. Buffers are limited in their buffer capacity, that is, the amount of a strong acid or strong base that can be added before the pH changes by 1 pH unit.

Buffers are very important to many industrial and natural processes. For example, controlling the pH of blood is essential to human health. The pH of blood is normally 7.40 ± 0.05, and good health depends on the ability of buffers to maintain the pH of blood within this narrow range. If the pH falls below 7.35, a condition known as acidosis occurs; increasing pH above 7.45 leads to alkalosis. Both these conditions can be life threatening. Two buffer systems, H_2CO_3/HCO_3^- and $H_2PO_4^-/HPO_4^{2-}$, control the pH of the blood.

Lewis Acid-Base Theory

In the early 1930s Gilbert Lewis, an American chemist, proposed a more general acid-base theory that is based on sharing electron pairs rather than proton transfers. A Lewis acid is a substance that can accept a pair of electrons to form a new bond, and a Lewis base is a substance that can donate a pair of electrons to form a new bond. All Arrhenius and Brønsted-Lowry acids and bases are Lewis acids and bases. However, Lewis acid-base theory is more general because a Lewis base can donate an electron pair to something other than H^+. For example, the gas **phase** reaction of NH_3 with BF_3 is a Lewis acid-base reaction.

phase: homogeneous state of matter.



(24)

Solvent System Acid-Base Theory

Another acid-base theory that is useful for solvents other than water was postulated by American chemist Edward Franklin in 1905. It makes use of the autoionization of solvents, and defines an acid as a solute that produces the positively charged species of the solvent and a base as a solute that produces the negatively charged species of the solvent. In the case of the autoionization of water (equation 18) H_3O^+ is the acid and OH^- is the base. For the nonaqueous solvent, liquid ammonia, the autoionization gives

$$NH_3\ (l) + NH_3\ (l) \rightleftarrows NH_4^+ + NH_2^- \qquad (25)$$

so an acid in liquid ammonia is any solute that produces NH_4^+ and a base in liquid ammonia is any solute that produces NH_2^-. An example of an acid-base reaction in liquid ammonia is

$$\underset{\text{acid}}{NH_4Cl} + \underset{\text{base}}{NaNH_2} \rightarrow \underset{\text{salt}}{NaCl} + \underset{\text{ammonia}}{2\ NH_3} \qquad (26)$$

Note that liquid ammonia still falls within the Brønsted-Lowry definitions since NH_4^+ is a proton donor and NH_2^- is a proton acceptor.

Summary

The Brønsted-Lowry theory, which defines acids as proton donors and bases as proton acceptors, covers all acid-base reactions in aqueous solution. The strength of acids and bases is related to the percent of their ionization in water. Strong acids and bases are 100 percent ionized, whereas weak acids and bases are less than 5 percent ionized. There are a number of salts that have acidic or basic properties in solution. For example, baking soda, $NaHCO_3$, can be used as an antacid because the bicarbonate ion, HCO_3^-, is a strong enough conjugate base to combine with H_3O^+ to give carbonic acid.

$$HCO_3^-\ (aq) + H_3O^+\ (aq) \rightarrow H_2CO_3\ (aq) + H_2O\ (l) \qquad (27)$$

The pH scale is a convenient way to represent the acidity or basicity of dilute acid and base solutions. Pure water has a pH of 7; acidic solutions have pH values < 7 and basic solutions have pH values > 7. Each change of one unit of pH is a tenfold change in acidity. Acid-base indicators, such as litmus and phenolphthalein, can be used to measure whether a solution is acidic or basic. A natural "universal indicator," red cabbage extract, can be used to determine the pH within 2 pH units. A buffer contains equal amounts of either a weak acid and its conjugate base or a weak base and its conjugate acid.

SEE ALSO ARRHENIUS, SVANTE; BASES; BRØNSTED, JOHANNES NICOLAUS; CHEMICAL REACTIONS; LEWIS, GILBERT N.; SOLUTION CHEMISTRY.

Melvin D. Joesten

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Internet Resources

More information available from <http://www.visionlearning.com/library/index.htm>.

"CHEMystery: An Interactive Guide to Chemistry." Available from <http://library.thinkquest.org/3659/acidbase/>.

Acid-Rain ***See Atmospheric Chemistry.***

Acne Medication

Acne is a skin condition in which pimples (comedones) appear on the skin, usually on the face, chest, or back. Adolescents and young adults are most often afflicted. Acne tends to be more severe in males; however, with females, acne may persist into adulthood.

Causes and Types of Acne

The skin has hair follicles that each contains a hair shaft and an oil gland. The oil glands continuously produce and secrete oil to lubricate and protect the skin. However, when dead skin cells and oil (sebum) build up inside the follicle and close off the follicle's pore, pimples appear, in the form of either blackheads or whiteheads. If the plugging material protrudes from the opening at the surface of the skin, this plug of oil and dead cells darkens, forming blackheads; if the plugging material does not protrude, whiteheads form. This type of acne is referred to as comedonal. When the accumulated material of a closed-off pimple causes the follicular wall to rupture, an internal inflammatory reaction occurs, causing oil, dead cells, and bacteria to spill onto the skin. The skin around the pore becomes red and inflamed, and the result is inflammatory acne. When white blood cells infiltrate the area to repair the inflammation, papules, nodules, and cysts may develop. Papules form near the surface of the skin, whereas nodules and cysts are caused by inflammation deeper in the skin.

In the past many persons attributed abnormally high oil secretion and the development of acne to the afflicted individual's diet and hygiene. However, current research suggests that oil secretion is under genetic control, primarily related to the ability of androgenic hormones to stimulate oil secretion. The bacterial species *Propionibacterium acnes* is believed to play a role in converting acne into an inflammatory condition. Stress and the use of certain cosmetics may also be contributing factors.

Treatment of Acne

There are many ways to treat acne. Gentle washing of the face is important because it helps to remove accumulated oil, bacteria, and dead cells on the skin's surface. Other treatments help to unclog pores, kill bacteria, or minimize oil. Products that help to open up pores include mild cleansers, scrubs, exfoliants, and masques. All of these are available without a prescription. Exfoliants remove the outer layer of skin, thus opening pores. These agents, as well as astringents and toners, help to wipe away excess oil. Antibacterial agents are used to kill bacteria. The most common mild antibacterial agent is benzoyl peroxide. It is available in the form of creams or lotions that are applied to affected areas, and may even be found in some cleansers. Other antibacterial agents available by prescription include topical antibiotics such as **erythromycin**, clindamycin, and sulfacetamide, and oral antibiotics such as tetracycline, doxycycline, minocycline, and sulfa drugs.

A female with untreated acne on her face. Several prescription and nonprescription drugs are used to effectively treat acne.

erythromycin: antibiotic used to treat infections

Benzoyl peroxide. Benzoyl peroxide encourages peeling of the outermost layer of the skin and, as mentioned previously, is a mild bactericidal agent. It kills bacteria by virtue of its oxidizing properties. It is often included in prescription acne medications, and in nonprescription acne products such as gels, lotions, and cleansers. It may be used alone or with other treatments. At even low concentrations (2.5–10%), benzoyl peroxide diminishes the population of *Propionibacterium acnes.* The most common adverse effects are dry skin and bleaching of the skin.

Retinoids. The term "retinoid" refers to retinol or other closely related derivatives, either natural or synthetic. Retinoids may or may not have retinol-like (**vitamin** A–like) activity. Retinoids affect epithelial cells by binding to **receptors** inside these cells, inducing alterations in the **transcription** of genes. Retinoids enhance the **synthesis** of some proteins, such as proteins that serve as receptors for certain hormones and growth factors, and reduce the synthesis of others. Some of the most commonly prescribed treatments for acne—tretinoin, isotretinoin, and adapalene—are retinoids. (See Table 1.)

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

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

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

synthesis: combination of starting materials to form a desired product

Tretinoin became available as a topical treatment for acne in the United States in 1971. Tretinoin is also known by its chemical name, all-*trans*-retinoic acid. It increases the turnover of skin cells at the surface of the hair follicle. This leads to the extrusion of comedones. Side effects include local skin irritation and increased sun sensitivity. Newer preparations of tretinoin, designed to achieve slow absorption of the drug into epithelial cells, cause less skin irritation than forms available initially. Improvement in acne may not be noticeable until two to three weeks after treatment begins.

In 1982 the Food and Drug Administration (FDA) approved the oral use of isotretinoin (Accutane) for the treatment of severe nodulocystic acne that has not responded to antibiotics. This drug is not active topically. As the name suggests, isotretinoin is an **isomer** of tretinoin. The only structural difference between the two molecules lies in the spatial arrangement of the atoms around one carbon-carbon double bond. Isotretinoin has the chemical name 13-*cis*-retinoic acid. Through mechanisms not well understood, it decreases the size of the sebaceous glands and inhibits closure of the pore. These actions may diminish the ultimate formation of cysts. As is

isomer: molecules with identical compositions but different structural formulas

Table 1. Generic and brand names of some commonly prescribed acne medications.

GENERIC AND BRAND NAMES OF SOME COMMONLY PRESCRIBED ACNE MEDICATIONS

Brand Name	Generic Name
Desquam-E, Benzac W, Benzagel, Clinac BPO, Triaz	benzoyl peroxide
Retin-A, Renova, Avita	tretinoin
Accutane	isotretinoin
Differin	adapalene

SOURCE: Data obtained from *http://www.healthsquare.com/drugmain.htm*

the case with other retinoids, arachidonic acid release from macrophages is inhibited. This may account for the anti-inflammatory effects of retinoids. Isotretinoin's anti-acne effects can last for months to years following a twenty week course. And, unlike antibiotic treatments, treatment with isotretinoin does not promote antibiotic-resistant bacteria.

Reservations toward the use of isotretinoin (Accutane) are related to its severe side effects. Any of the retinoids, including vitamin A, can have severe side effects. Some of the symptoms of hypervitaminosis A are the same as the major toxic effects associated with the therapeutic use of retinoids. When retinoids are applied to the skin, few systemic side effects occur. For isotretinoin, which is administered orally, side effects are much more common. Among those reported are skin blistering, skin fragility, hair loss, headache, nausea, vomiting, visual disturbances, and increased levels of triglycerides and decreased levels of high density lipoproteins in blood plasma. Furthermore, because isotretinoin can cause severe birth defects, including physical abnormalities and mental retardation, a female patient taking it must not become pregnant. Female patients must obtain a negative serum pregnancy test before treatment can begin, and written consent forms must be signed. These patients should also not become pregnant for some time after the drug has been discontinued. In 1998, as a result of medical reports associating Accutane use with depression and suicide, the FDA issued new safety information regarding isotretinoin.

Newer retinoids. Medical chemists are often able to modify the structure of a drug that has unwanted side effects or problems making it difficult to administer. Even slight structural changes may result in an improved pharmacological agent that requires lower dosing, or has fewer side effects, or both. The development of adapalene is an example. A better retinoid might have enhanced stability, enhanced anti-inflammatory effects, or result in decreased skin irritation. The naphthoic-acid derivative adapalene, developed in the 1990s, works better and with less local skin irritation than earlier retinoids. The reduced side effects are attributed to the selectivity of adapalene for **nuclear** retinoic acid receptors within follicular epithelial cells. Although many persons will have acne during their teen years, effective treatment is available. SEE ALSO RETINOL.

nuclear: having to do with the nucleus of an atom

Jennifer L. Powers

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Internet Resources

Information available from <http://www.accutaneaction.com>.

Information available from <http://www.differin.com>.

Information available from <http://www.fda.gov>.

Information available from <http://healthsquare.com/drugmain.htm>.

Actinides

The actinide elements (atomic numbers 89 through 103) involve the filling of 5f orbitals. All actinides are radioactive, but only uranium and the lighter actinides have half-lives long enough to be present in Earth's environment. The heavier actinides are produced by **nuclear** reactions and some have very short half-lives. The actinides also undergo a radius **contraction** as do the **lanthanides** with an increasing **atomic number**. They are characterized by variable **oxidation** numbers, but the importance of the +3 state and the similarities to lanthanides increase for heavier elements. American chemist Glenn Seaborg is credited with revising the Periodic Table so actinides were placed under lanthanides. SEE ALSO Actinium; Americium; Berkelium; Einsteinium; Fermium; Lawrencium; Mendelevium; Neptunium; Nobelium; Plutonium; Protactinium; Rutherfordium; Seaborg, Glenn Theodore.

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nuclear: having to do with the nucleus of an atom

contraction: the shortening of a normal trend of a quantity, in this case the radius

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

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

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

Actinium

MELTING POINT: 1,050°C
BOILING POINT: 3,200°C
DENSITY: 10.07 g/cm^3
MOST COMMON IONS: Ac^{3+}

Actinium has thirty-six **isotopes**, all of which are radioactive and which range in mass number from 209 to 234. The longest-lived isotope has a mass number of 227 and a half-life of 21.8 years. Actinium was discovered in **pitchblende** in 1899 by French chemist André-Louis Debierne, a member of the Curie laboratory. He named it *actinium*, using the Greek word *aktis*, meaning ray. It was discovered independently by Friedrich Giesel in 1902. Actinium in its ground state has an (outer orbital) electronic configuration of $5f^0 6d7s^2$. Actinium exists in an **oxidation** state of 3+ in solution and in its compounds. The isotope ^{227}Ac is found in uranium ores in concentrations of approximately 0.15 mg per ton of pitchblende, and at lower concentrations, in thorium ores. Pure actinium forms a silvery-white **metal** that has a face-centered structure near its melting point.

In 1945 Glenn Seaborg proposed that actinium was the first member of a family of fifteen elements (the "actinides"), characterized by the possession of the $5f$ orbitals. His proposal was based on the similarity of the chemistry of actinium to that of lanthanum (**atomic number** 57), which is the first member of the fifteen elements of the trivalent **lanthanide** family. Actinium is somewhat more basic than lanthanum but, like lanthanum, forms compounds that have strongly ionic bonds. Many actinium compounds are

89
Ac
ACTINIUM
227

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

pitchblende: mineral that is the principal ore of uranium

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

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

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

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

isostructural: relating to an arrangement of atomic constituents that is geometrically the same although different atoms are present

isostructural with the corresponding compounds of lanthanum, due to the similarities in radii and electronic structures among the two set of compounds. Due to the short half-lives of the isotopes of actinium, no significant uses have been developed for these isotopes. SEE ALSO BERKELIUM; EINSTEINIUM; FERMIUM; LAWRENCIUM; MENDELEVIUM; NEPTUNIUM; NOBELIUM; PLUTONIUM; PROTACTINIUM; RUTHERFORDIUM; SEABORG, GLENN THEODORE; THORIUM; URANIUM.

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Active Site

Enzymes play a vital role in the majority of biochemical reactions. Not only do they allow for life as we know it, they demonstrate remarkable specificity in many cases. How do enzymes work on only one chemical process, whereas hundreds of perhaps similar processes occur in the same general vicinity? Protein structure in general provides the answers. The primary, secondary, and tertiary structures of a protein all serve to direct the specific activity of an enzyme, but the region where the specific reaction is catalyzed is referred to as the active site.

If one could place a thin skin on the surface of an enzyme, the active site would invariably look like a pocket or cave in the surface. This structural feature is the reason why many textbooks show the mechanism of enzyme specificity as a lock-and-key model. The substrate, the molecule on which the enzyme acts, is the key that fits into the enzyme, which is the lock. Like a lock, only the correct key fits into it.

intermolecular force: force that arises between molecules; generally it is at least one order of magnitude weaker than the chemical bonding force

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

hydrogen bond: interaction between H atoms and lone pair electrons that constitutes hydrogen bonding

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

covalent bond: bond formed between two atoms that mutually share a pair of electrons

Looking at a more detailed perspective than is provided by this model, one can see that the selectivity of the active site is associated with its geometry. **Intermolecular forces** are present between the substrate and the components of the enzyme that are present in the active site.

For example, in order for **hydrogen bonding** to be able to take place, specific atoms must be present, as shown in Figure 1. In enzymes, normally there is either an O-H bond or an N-H bond when hydrogen bonding occurs. The other component of the **hydrogen bond** is a lone pair of electrons on either a nitrogen or oxygen. The strength of this interaction depends on the specific geometry present. The atoms must be both close enough to each other and in the correct direction from each other. Essentially, a hydrogen-bonding interaction requires that the three atoms involved form a straight (or nearly straight) line.

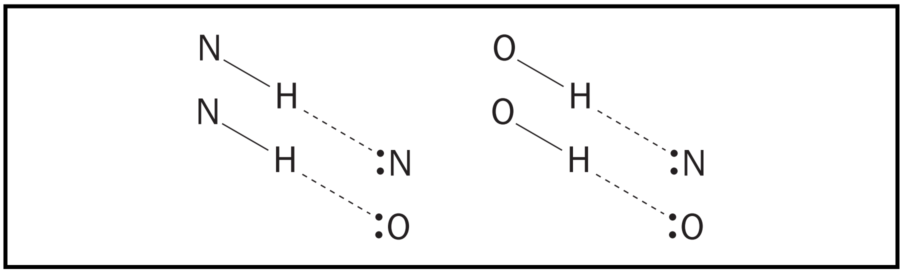

Figure 1. Atoms necessary for hydrogen bonding.

As there are many different types of active sites, it would be impossible to examine all of them here, but we can consider one important class of active sites, those that include **metal** ions. The inclusion of the metal ion in the enzyme may either be from strong coordinate **covalent bonds**, or via a looser association in the active site. When the metal is tightly bound, the protein is called a **metalloenzyme**. When the binding is not covalent, a metal-activated enzyme results. In either case, the metal ion is likely to be an important part of the active site.

One role that metal ions play in the active site of enzymes is to stabilize the charges that may be present. For example, the enzyme carbonic anhydrase, which plays the vital role of assisting the transport of carbon dioxide in the blood, is a metalloenzyme that includes zinc ions, Zn^{2+}. This enzyme catalyzes the reaction of carbon dioxide with water to form hydrogen carbonate ions

$$CO_2 + H_2O \rightarrow HCO_3^- + H^+$$

To speed this reaction, the zinc ion interacts with the water molecule to form a hydroxide, as shown in Figure 2. The small highly positively charged zinc ion is well suited to stabilize the negative charge of the hydroxide ion. Once formed, this ion reacts with carbon dioxide to form the hydrogen carbonate ion, which is released, and the Zn^{2+} is now ready to catalyze another reaction.

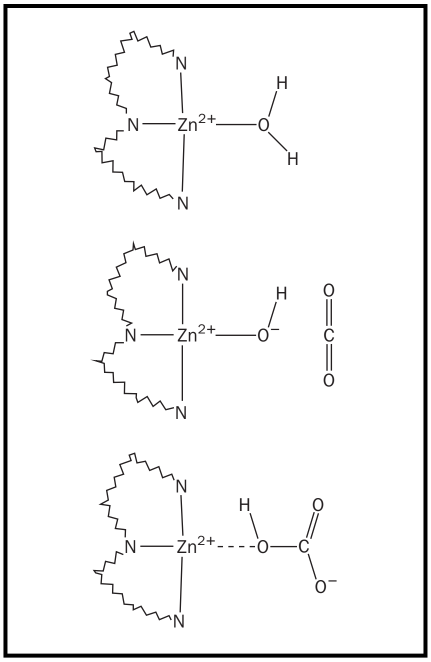

Figure 2. Zinc ions interacting with water to form a hydroxide.

metalloenzyme: a protein enzyme that contains at least one metal atom, often in an active site of the protein

Most active sites operate in ways that are somehow similar to those of this example. Portions of the enzyme in the active site bind to the substrate, facilitating its reaction, and then they release the product. SEE ALSO Enzymes; Proteins; Residue; Substrate.

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Adenine *See Nucleotide.*

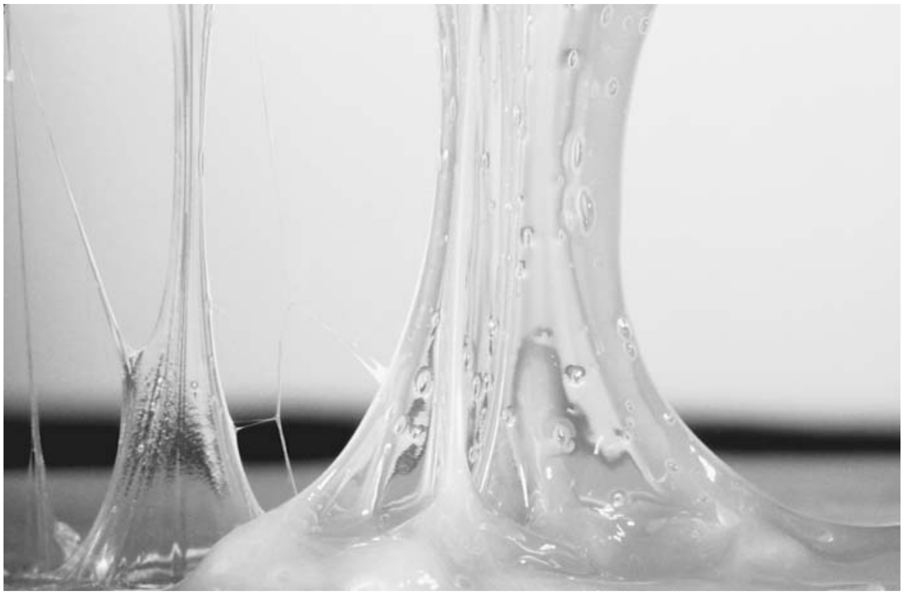
Adhesives

An adhesive is a substance that sticks to the surface of an object such that two surfaces become bonded. A typical home improvement store carries many different adhesives for many different applications. Why are there so many adhesives? The answer is found in examining how an adhesive works and, in particular, what happens at the molecular level. The interaction of molecules is known as intermolecular bonding, or secondary bonding. Primary bonding, also known as intramolecular bonding, is the interaction of atoms within a molecule and includes covalent and polar covalent bonding. Secondary bonding includes dipole–dipole bonding (the interaction of molecules that have a permanent net dipole moment) and **hydrogen bonding** (an interaction that occurs when a hydrogen atom is bonded to an N, O, or F atom in a molecule).

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

Adhesives cure when the small resin molecules (mers) join together to form extremely large molecules known as polymers. For example, one of

Some adhesives, such as this wood adhesive, are used only with specific substrates because of the cure time needed to allow for good bonding.



the simplest polymers is polyethylene. The mer (basic building block of the polymer) is ethylene, $H_2C{=}CH_2$. The addition of an initiator (R·) causes the formation of the radical $RCH_2CH_2\cdot$. A radical is a species that has an unpaired electron and is very reactive because it seeks the source of electrons. This radical will attach the ethylene mer (the double bond in ethylene is rich in electrons) to start a chain reaction that continues until very large polymer molecules form. This and other forms of polymerization processes are the basis for the formulation of polymers. This process is known as curing when dealing with adhesives.

electronegative: capable of attracting electrons

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

Two criteria must be met in order for a molecule to possess a permanent net dipole moment: (1) an unequal sharing of electrons within the molecule such that one or more intramolecular bonds has a partial positive end and a partial negative end, and (2) a geometry such that the vector sum of the individual dipole moments does not equal zero. The ability of an atom within a molecule to attract electrons is known as electronegativity, a concept proposed by Linus Pauling who established a table of relative electronegativities. In Pauling's table, fluorine is the most **electronegative** element and is given the value of 4.0. The greater the difference in electronegativity between two atoms within a molecule, the larger is the dipole moment in that bond. Because the bond between two atoms having unequal electronegativities has a partial positive end and a partial negative end, it is said to be a polar bond. If the geometry of the molecule is such that the vector sum of all of the dipole moments does not equal zero, then the molecule is polar. The electronegativities for carbon and oxygen are 2.5 and 3.5, respectively; therefore, the carbon–oxygen bond is a polar bond. A carbon dioxide molecule has two carbon–oxygen bonds; however, its geometry is such that the vector sum of the two dipole moments equals zero, and thus carbon dioxide is a **nonpolar** molecule. The electronegativity of hydrogen is 2.1, thus a hydrogen–oxygen bond would be polar. A water molecule has two hydrogen–oxygen bonds. The geometry of a water molecule (the H–O–H bond angle is 104.5°) is nonsymmetrical, hence the vector sum of the dipole moments is not equal to zero and water is a polar molecule.

Polar molecules will attract other polar molecules because of their net dipole moments. Water molecules, however, have an additional **attraction** for one another, based on hydrogen bonding. This attraction is so strong that, although water is a small molecule and small molecules tend to be gases, water is a liquid at room temperature. This aspect of the chemistry of water demonstrates that hydrogen bonding is a relatively strong force that can hold molecules together.

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

So how does this relate to the many types of adhesive products that exist? In order for an adhesive to bond (hold together) two surfaces (substrates), there must be several types of interaction between the adhesive and both substrates. The first type of interaction is that the adhesive must wet the substrate, meaning that the adhesive must spread itself out into a film that covers the substrate surface. In order for this to happen, the adhesive must have a low enough viscosity so that it will flow. Viscosity is the resistance of a liquid to flow. Water has a low viscosity whereas honey has a high viscosity. Because viscosity is temperature dependent, the application of a cold adhesive to a substrate, or the application of an adhesive to a cold substrate, may result in poor wetting. Another factor that affects wetting is the relative strengths of cohesive forces (between like molecules, such as two adhesive molecules) and those of adhesive forces (between unlike molecules, such as an adhesive molecule and a substrate molecule). If the cohesive forces among adhesive molecules are weaker than the adhesive forces between the adhesive molecules and the substrate surface, then the adhesive molecules will spread out over the substrate and wet its surface. An adhesive that has a relatively low viscosity and is able to wet the substrate surface will flow into any tiny cracks or pores on the substrate surface, thus promoting what is known as mechanical bonding. Mechanical bonding increases the strength of an adhesive bond and, as a result, a forced separation of the two substrate surfaces is more apt to tear the substrate surfaces.

Mechanical bonding is one of several ways that an adhesive bonds substrates. All surfaces, except those that are highly polished, have pores. If the adhesive flows into these pores and then polymerizes, a mechanical bond is formed. It is similar to placing a wick into liquid candle wax. Once the wax solidifies the wick can not be easily removed. A mechanical bond has formed.

Because the interactions of adhesive molecules with substrates are so critical, it makes sense that some adhesives would be more appropriate for a specific substrate than others. Adhesives are designed for specific applications. For example, adhesives known as "super glues" (cyanoacrylates) are useful around the home in the bonding of common substrates (e.g., dishes, toys, etc.), which can take place in a matter of seconds. Yet their usefulness is limited when bonding wood because the cure time (the time it takes for an adhesive to undergo polymerization and become capable of holding the two substrates together) in this instance is much longer. Cyanocrylates tend to be brittle thus they are vulnerable to impact and dramatic changes in temperature. To reduce these shortcomings, small amounts of finely ground rubber has been used as filler. The rubber introduces flexibility thus reducing brittleness. In addition, cyanocrylates are attacked by polar solvents. Polar solvents will weaken cured cyanocrylate bonds over time. Therefore, applications involving water, alcohols, or other polar solvents should be avoided. Polymerization is the reaction of small molecules combining to form very

Table 1. Common adhesives and their uses.

TYPES OF ADHESIVES

Adhesive Type	Sources/Properties	Common Uses
Animal glue	Obtained from animal byproducts such as bones, blood, and hooves	Binding of abrasives in sandpaper and other grinding materials
Casein	Main protein in milk	Labels on beer bottles that do not come off in ice water, yet are recyclable
Starch	From corn and maize	Corrugated cardboard bonding
Natural rubber	Not "sticky enough" by itself but is used as an additive in other adhesives	Self-adhesive envelopes and other pressure-sensitive adhesives; adhesives that bond to substrates on contact (like tapes)
Butyl rubber/isobutylene	It is elastomeric—it stretches	Additive for hot-melt adhesives, window sealants, and pressure-sensitive adhesives
Amino resins	Water-soluble adhesives	Bonding of layers in plywood and the bonding of particles in particle board
Polyurethane	A flexible adhesive	Bonding soles to the bodies of shoes; also used in food packaging
Polyvinyl acetate	Common "white" glue	Book bindings and labels
Polyolefin/ethylene copolymer	No solvents involved	Hot melts
Acrylates or anaerobic adhesives	Cure when air is removed	Adhesive used to keep nuts tight on bolts, such as those within ATMs and heavy machinery
Silicone	Both an adhesive and a sealant and only common adhesive that is based on silicon rather than carbon	Bathtub and shower sealants; also many car applications, such as oil pans and head gaskets

large molecules. The reason for the longer cure time in the bonding of wood has to do with chemical reactions (between adhesive and substrate) that affect the rate at which the cyanoacrylate molecules polymerize. A typical cyanoacrylate product is a low viscosity liquid that readily flows over a substrate's surface. When the cyanoacrylate molecules encounter a basic environment, the small molecules within the adhesive polymerize. Many common surfaces tend to be basic, so a cyanoacrylate adhesive works fine in these instances; wood, however, tends to have an acidic surface, and because an acidic environment will inhibit polymerization, cure time is increased.

Cyanoacrylates are not appropriate for the bonding of the steel parts of an automobile, because of the environments that the car will be exposed to. Those environments include such things as rain, variations in temperature, exposure to solvents (such as gasoline, oil, and windshield washer solution), ozone, **acid rain**, salt spray, and ultraviolet light from the Sun. (A more appropriate adhesive for car parts would be an epoxy-based adhesive.) Another example of a "special" adhesive would be the one used to attach a new rearview mirror in an automobile. Because the cured adhesive in this case will be exposed to wide variations in temperature and to an extremely large amount of ultraviolet light from the Sun for prolonged periods of time, an adhesive formulated specifically for these conditions should be used.

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

Finally, the strength and permanence of the bond formed between adhesive and substrate must be considered when one is selecting an adhesive. Most of the time it is desirable to have maximum strength and permanence; the very common Post-it note, however, is a counterexample. Its adhesive is neither strong nor permanent. The adhesive formulation that eventually led to the Post-it was initially considered a failure because of the adhesive's weakness. It was while singing in his church choir that Arthur Fry of the Minnesota Mining & Manufacturing Company (3M) envisioned a potential use for what seemed to be a useless material.

Table 1 lists some common types of adhesives and their uses. Because of the different possible substrates and combinations of substrates, and because adhesives are subject to such a range of environmental conditions, it is no wonder that there are so many types of adhesives on the market. However, if one has some knowledge of how adhesives bond to substrates and the types of substrates being bonded, the task of selecting adhesives will not be overwhelming. SEE ALSO Bonding; Pauling, Linus.

Daryl J. Doyle

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Adrenalin ***See Epinephrine*.**

Agricultural Chemistry

Agricultural chemistry must be considered within the context of the soil ecosystem in which living and nonliving components interact in complicated cycles that are critical to all living things. Carbon inputs from photosynthetic organisms ultimately provide the fuel for many soil organisms to grow and reproduce. Soil organisms, in turn, promote organic carbon degradation and catalyze the release of nutrients required for plant growth. The stability and productivity of agricultural ecosystems rely on efficient functioning of these and other processes, whereby carbon and nutrients such as nitrogen and phosphorus are recycled. Human-induced perturbations to the system, such as those that occur with pesticide or fertilizer application, alter ecosystem processes, sometimes with negative environmental consequences.

Inorganic Components of the Agricultural Ecosystem

Soil is the primary medium in which biological activity and chemical reactions occur. It is a three-**phase** system consisting of solid, liquid, and gas. Approximately 50 percent of the volume in a typical agricultural soil is solid material classified chemically as either organic or inorganic compounds. Organic materials usually constitute 1 to 5 percent of the weight of the solid phase. The remainder of the soil volume is pore space that is either filled with gases such as CO_2 and O_2, or water.

phase: homogeneous state of matter

Surface area and charge characteristics of the inorganic portion of the solid phase control chemical reactivity. Soil particles are classified based on their size, with sand-sized particles having diameters of 2 to 0.05 millimeters (0.08 to 0.002 inches) and silt-sized particles from 0.05 to 0.002 millimeters (0.002 to 0.00008 inches). Clay-sized materials of less than 0.002 millimeters (0.00008 inches) in diameter have the largest surface area per unit weight, reaching as much as 800 meters (2,625 feet) squared per gram. Because of large surface areas, clay-sized materials greatly influence the sorption of chemicals such as fertilizers and pesticides and play a major role in catalyzing reactions.

Crystalline layer silicates or phyllosilicates present in the clay-sized fraction are especially important because they function as ion exchangers. Most phyllosilicates have a net negative charge and thus attract cations. This cation exchange capacity (CEC) controls whether plant nutrients, pesticides, and other charged molecules are retained in soil or if they are transported out of the soil system. In contrast, aluminum and iron oxides also present in the clay-sized fraction typically possess a net positive charge or an **anion** exchange capacity (AEC). Soils in temperate regions are dominated most often by solid phase materials that impart a net CEC, whereas soils in tropical regions often contain oxides that contribute substantial AEC.

anion: negatively charged chemical unit, like Cl^-, CO_{32}^-, or NO_3^-

Organic Components of the Agricultural Ecosystem

Organic materials contained within the solid phase, although only a small percentage of the total soil weight, are extremely important in controlling chemical and physical processes in soil. Organic matter exists in the form of recognizable molecules such as proteins and organic acids, and in large polymers called humic materials or humus. Humus is dominated by acidic **functional groups** ($-OH$ and $-COOH$) capable of developing a negative charge and contributing substantial CEC. These large polymers possess a three-dimensional conformation that creates **hydrophobic** regions important in retaining nonionic synthetic organic compounds such as pesticides. Nonionic pesticides partition into these hydrophobic regions, thereby decreasing off-site movement and biological availability (see Figure 1).

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

hydrophobic: a part of a molecule that repels water

A wide variety of organisms live in soil, including microorganisms not visible to the naked eye such as bacteria, fungi, protozoa, some algae, and viruses. Bacteria are present in the largest numbers, but fungi produce more **biomass** per unit weight of soil than any other group of microorganisms. Much of agricultural chemistry as it relates to nutrient cycles, pesticide transformation, plant growth, and organic matter degradation involves the participation of microorganisms. Microorganisms produce both intracellular and extracellular enzymes that increase reaction rates, oxidize and reduce organic and inorganic compounds, and synthesize organic molecules that modify soil chemical and physical properties.

biomass: collection of living matter

Additional organisms in soil such as insects, nematodes, and earthworms also alter the soil ecosystem in a manner that directly or indirectly affects chemical reactions. These organisms physically process plant-derived organic materials prior to biochemical degradation by microorganisms. Nutrient release from organic materials is thus accelerated because the meso- and macrofauna expose more organic matter surface area to microbial breakdown and redistribute such materials in soil to areas of intense microbial ac-

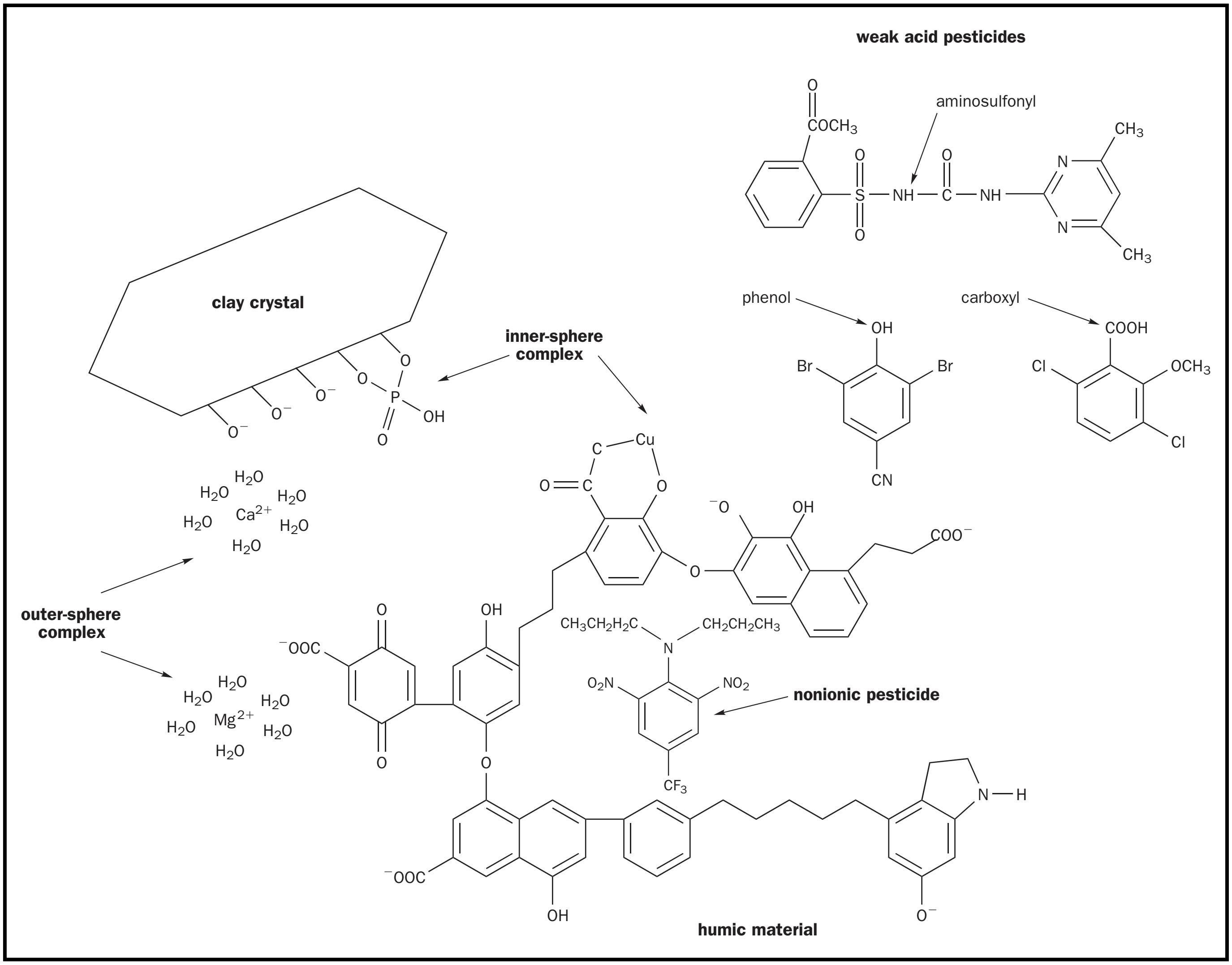


Figure 1. Interaction of ions and organic pesticides with the clays and humic materials in soil. Ions interact with clay crystals by binding directly, as in the case of the inner-sphere complex shown for PO_4^{3-}, or electrostatically in an outer-sphere mechanism, as shown for hydrated Ca^{2+}. Like clays, humic materials also have a net negative charge or a CEC that allows for inner-sphere complexation as shown for Cu^{2+} or outer-sphere interaction as shown for hydrated Mg^{2+}. In addition, humic materials will interact with nonionic pesticides by partitioning them into hydrophobic regions within the large polymeric molecule. Neither clays nor humic materials have a strong affinity for weak acid pesticides containing phenolic hydroxyls, carboxyl groups, or aminosulfonyl linkages.

tivity. In addition, bioturbation may also cause physical changes to the soil structure that increase pore space or modify water movement. Changes in O_2 concentration or soil water content will control biotic and abiotic reactions, altering rates of nutrient cycling and organic matter degradation.

Plant roots also modify soil by producing a zone of intense biological activity called the rhizosphere. This is a region of soil influenced by the root, most often delineated by comparing microbial numbers at greater distance from the root surface. Carbon compounds exuded or sloughed off from roots are used as a food source by microorganisms, thereby causing increased growth and activity. Microbial numbers above those of the bulk soil, which displays no root influence, indicate that the rhizosphere extends to 5 millimeters (0.2 inches) or less. Rhizosphere microorganisms that capitalize on carbon from the plant root interact physically and biochemically with the root, potentially producing positive or negative effects on plant growth.

Soil Chemistry

covalent bond: bond formed between two atoms that mutually share a pair of electrons

Biological availabilities and transport phenomena of ions and molecules in soil are controlled by the type of bonding that occurs with the solid phase. Ions such as those typically formed when amending soils with inorganic fertilizers interact with high surface area clay and humic colloids to form either outer- or inner-sphere complexes (see Figure 1). Outer-sphere complexes result when ions, electrostatically attracted to an oppositely charged colloidal surface, retain their shell of hydrating water molecules. These loosely held ions satisfy the excess positive or negative charge of the colloid, but are separated from the colloid's surface by one or more layers of water. In contrast, inner-sphere complexes form when the ion loses its hydration water to form a much stronger **covalent bond** with the colloid. Nutrient ions held in outer-sphere complexes are plant-available because they may be exchanged with ions of the same charge, but nutrients held by an inner-sphere mechanism are not available until the covalent bond is broken.

Most soils contain a net CEC often reported in centimoles of charge per kilogram of soil (cmol_c/kg). Biological and physical characteristics of the soil are controlled by the amount of CEC and the specific cations involved. Soils dominated by high surface area clays or humus display the highest CECs, whereas soils with large amounts of sand or silt, and only small amounts of humus, exhibit much lower CECs. Highly charged cations with small hydrated radii such as Al^{3+} are more tightly held on the CEC and less likely to exchange than larger, less highly charged cations such as Na^+. This general relationship is superseded when a specific inner-sphere complex forms such as between Cu^{2+} and humus, or K^+ and clay. An even more dramatic example is that of two plant nutrients, NO_3^- and PO_4^{3-}. Negatively charged NO_3^- readily leaches out of soil, but PO_4^{3-} is retained quite strongly because it forms an inner-sphere complex (see Figure 1).

The percentage of the CEC occupied by specific cations influences soil pH and associated characteristics relevant to plant growth and soil biological activity. Only the most strongly held cations remain in soils in high rainfall areas. Al^{3+} dominates the CEC, hydrolyzing when released from the solid phase to the soil solution to form acidic soils with pH values often below 5.

$$Al^{3+} + H_2O \longleftrightarrow AlOH^{2+} + H^+$$

In contrast, soils located in lower rainfall areas accumulate less tightly bound cations such as Ca^{2+}, Mg^{2+}, K^+, and Na^+ and have higher pH values between 5 and 7. In the most arid regions, large amounts of OH^--generating sodium and calcium salts accumulate, causing soil pH values to exceed 7. Plant growth is optimal in soils having pH values between 5.5 and 6.5 because aluminum toxicity occurring at lower pH values, and nutrient limitations caused by higher pH values, are avoided.

Soil Microbiology and Biochemistry

Biochemical transformations catalyzed largely by microorganisms are required for the sustained productivity of all ecosystems. Nutrients sequestered in organic materials and added in the form of fertilizers are cycled by mi-

Protesters pulling up genetically modified crops from a field in Banbury, U.K., during the 1990s. Crops are genetically modified to increase productivity and to produce chemicals, among other uses.

croorganisms in their quest for energy, reducing equivalents, and carbon. Microorganisms grow and reproduce by oxidizing organic or inorganic materials, thereby releasing electrons. The electrons are passed down a series of carriers aligned in a thermodynamic gradient designed to capture energy in the form of **adenosine triphosphate (ATP)**. Additional electrons originating from organic or inorganic materials are used to provide reducing equivalents necessary for synthesizing cell constituents. Carbon for cell growth is obtained from the organic materials being oxidized or captured in the form of CO_2 if inorganic materials are being oxidized.

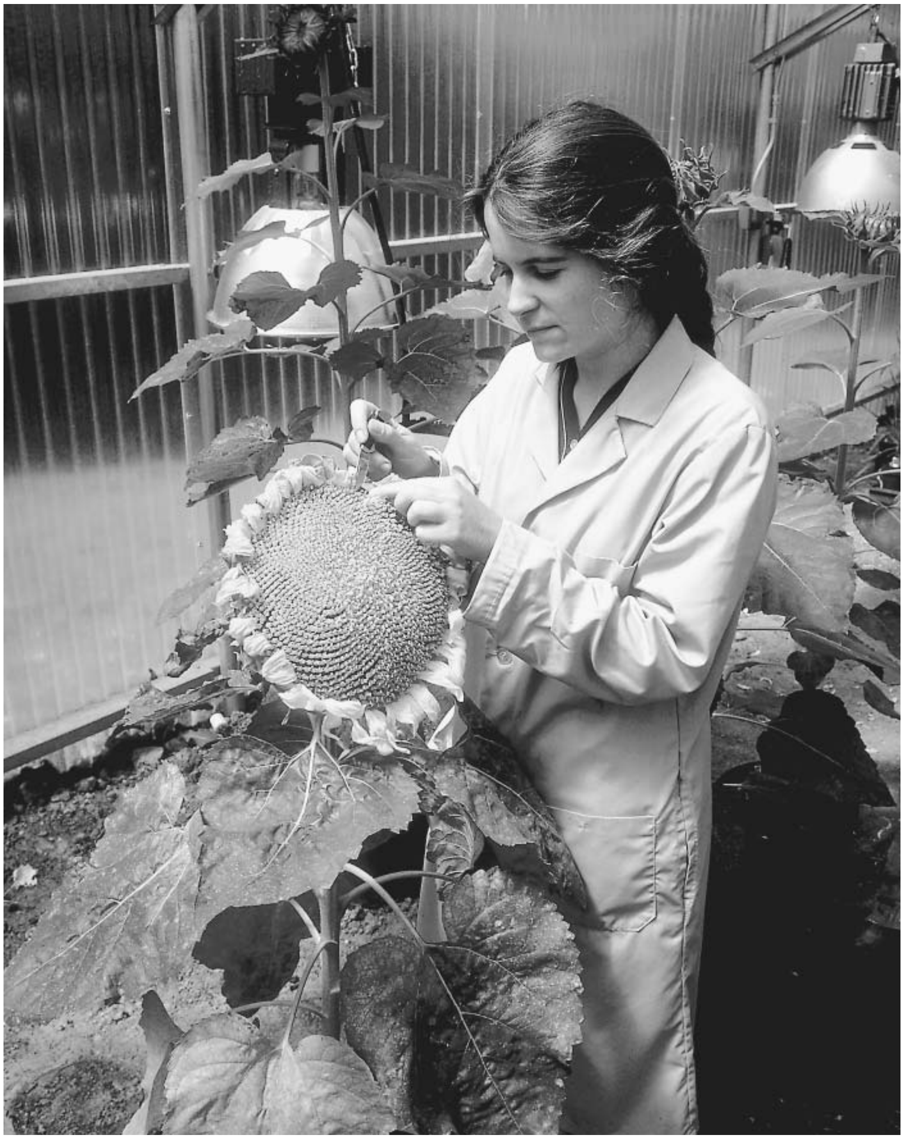
Reduction-**oxidation** processes are therefore central to agricultural chemistry because oxidation of the electron source and reduction of the electron sink profoundly modify the respective element's chemical characteristics, and thus its behavior and biological availability in the environment. For example, microbial oxidation processes convert organic compounds to CO_2, a gas, and NH_4^+, a cation, to NO_3^-, an anion. Electrons obtained in these oxidations are passed on to a terminal electron acceptor. Microorganisms use terminal electron acceptors in a sequence that maximizes energy yield starting with O_2 and proceeding through NO_3^-, Mn^{4+}, Fe^{3+}, SO_4^{2-}, and finally CO_2, which upon reduction yield H_2O, N_2, Mn^{2+}, Fe^{2+}, H_2S, and CH_4, respectively.

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

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

Human Manipulation of Agricultural Ecosystems

Food and fiber production are typically optimized by carefully managing the agricultural ecosystem. Synthetic organic compounds are often applied



A laboratory technician at Sungene Technologies Lab in Palo Alto, California, is removing tissue from a sunflower plant for genetic engineering projects.

to control plant pests including weeds, insects, nematodes, and fungal pathogens. Pesticide fate is controlled by sorption to the solid phase and degradation rate. Because most soils have a CEC, cationic pesticides are so strongly held by soil that they are typically biologically unavailable. Weak acid pesticides containing carboxyl, phenolic hydroxyls, or aminosulfonyl functional groups are weakly retained by soil and thus most likely to leach or move off-site (see Figure 1). Weak bases, which may exist as positively charged or uncharged molecules, and nonionic compounds, are intermediate in their susceptibility to move off-site and cause environmental contamination. However, rapid degradation of some pesticides to form benign products eliminates the time available for transport, decreasing the potential for environmental problems. Both biotic and abiotic mechanisms catalyze **degradative** reactions, the rate of which is controlled by the pesticide's chemical structure.

degradative: relating to or tending to cause decomposition

With the advent of molecular techniques and the ability to transfer genes, an additional area of concern has emerged: the introduction of foreign genes into plant species for enhanced crop productivity. In addition, we have the ability to produce a variety of pharmaceutical chemicals in genetically modified plants using what has been termed "pharm crops." David Suzuki and Holly Dressel in *From Naked Ape to Superspecies* have commented on such genetic manipulations, addressing the risks of placing genes from one species into another. Not only is direct gene transfer from one living organism to another possible, but extracellular **DNA** preserved in soil systems is also potentially available for transfer, further increasing environmental risks.

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

Agricultural chemistry is most often linked to food and fiber production, specifically for human consumption. Jared Diamond in *Guns, Germs, and Steel* argues quite convincingly that it was our ability to domesticate crops and eliminate the need for hunting and gathering that allowed for the establishment of permanent settlements and the development of technologically advanced societies. The ensuing increase in human population has led to tremendous pressure to produce additional food from finite resources. Increased agricultural production, in combination with additional resource consumption and waste generation, has caused environmental degradation. By understanding key concepts in agricultural chemistry, we can utilize the soil resource to produce an adequate food supply and protect the environment. SEE ALSO FERTILIZER; HERBICIDES; INSECTICIDES.

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Air Pollution

Air pollution is the presence in the atmosphere of any substance at a concentration great enough to produce an undesirable effect on humans, animals, vegetation, or materials, or to significantly alter the natural balance of any ecosystem. Air pollutants can be solids, liquids, or gases, and can have local, regional, and global impacts.

At urban scales, air pollution is frequently referred to as photochemical smog. "Smog" is a contraction of the words "smoke" and "fog," and was originally used to describe air pollution caused by coal burning in London. Urban smog is photochemical because many of the chemicals found in urban air are formed by chemical reactions driven by sunlight. Among the many air pollutants in urban smog that are produced by photochemical reactions, one of the most abundant is ozone, O_3. In contrast to the ozone found in the upper atmosphere (stratospheric ozone), which protects the planet from **ultraviolet radiation**, ground level or tropospheric ozone is a lung irritant and a danger to human health. It is also responsible for crop damage and is suspected of being a contributor to forest decline in Europe

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

combustion: burning, the reaction with oxygen

and in parts of the United States. Ground level ozone and other photochemical pollutants are formed in urban atmospheres by the reactions of oxides of nitrogen (mainly NO and NO_2) in the presence of hydrocarbons. Oxides of nitrogen are byproducts of **combustion** processes. At the high temperatures generated during combustion, some of the N_2 and O_2 in air is converted to oxides of nitrogen and, in general, the higher the combustion temperature, the greater are the amounts of oxides of nitrogen produced. Hydrocarbons are emitted from natural sources and as a result of activities utilizing organic solvents, coatings, or fuel. These hydrocarbons and oxides of nitrogen participate in reactions that yield, not only ozone, but also aldehydes, hydrogen peroxide, peroxyacetyl nitrate ($C_2H_3NO_5$), nitric acid, and molecular species of low volatility that accumulate in fine particles suspended in the atmosphere. Although many of these constituents of photochemical smog have environmental impacts, fine particulate matter (PM) presents the greatest health endangerment in most urban areas.

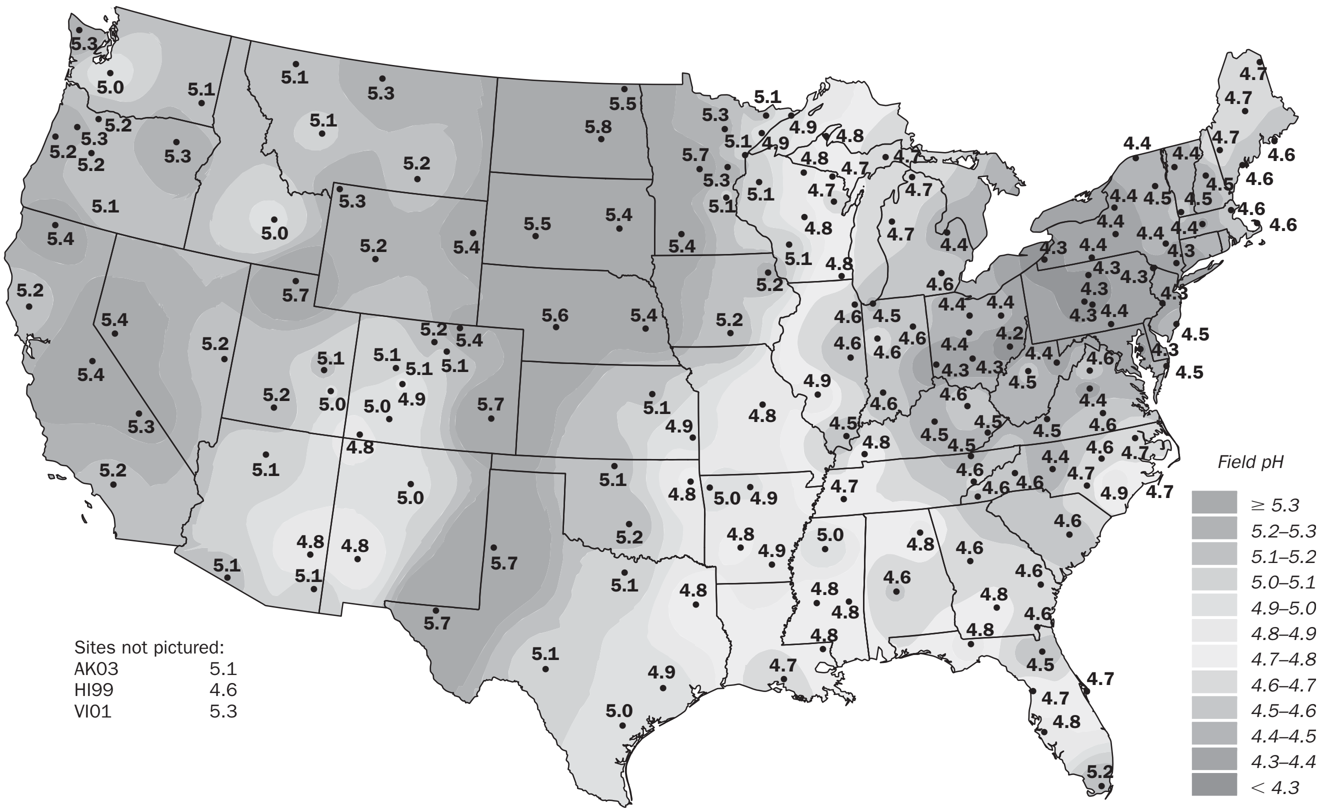
phase: homogeneous state of matter

Solid and liquid **phase** material in the atmosphere is variously referred to as particulate matter, particulates, particles, and aerosols. These terms are often used interchangeably, but all refer to particles with diameters between approximately 1 nanometer (3.9×10^{-8} inches) and 10 micrometers (39.4×10^{-5} inches) that remain suspended in the atmosphere for long periods. The greatest threats to health are associated with the smallest particles because they have the greatest likelihood of becoming deposited deep within the respiratory system.

Somewhat counterintuitively, particles of about 1 micrometer (39.4×10^{-6} inches) in size can remain suspended in the atmosphere much longer than gases. Particles much larger than 1 micrometer (39.4×10^{-6} inches) will, of course, quickly settle out of the atmosphere because of gravity. The smallest particles will coagulate and coalesce quickly, forming larger particles. But particles of approximately 1 micrometer (39.4×10^{-6} inches) in diameter do not grow as quickly as smaller particles and can remain suspended in the atmosphere for a week or more. It is not unusual, for example, for Saharan dust or particle plumes from Asia to be detected in the United States. Consequently, particulate matter is a continental to global scale air pollution problem.

Also, unlike ozone and other gas phase pollutants that are specific chemical species, particulate matter is a collection of chemical species defined mainly on the basis of particle size. The chemical constituents that make up particulate matter vary with particle size. Windblown dust is a main contributor to particles larger than 10 micrometers (39.4×10^{-5} inches) in diameter, whereas sulfates, nitrates, and organic compounds are the main constituents of smaller particles that can penetrate deeply into the respiratory system and engender health effects. Organic particles can be emitted directly as soot from combustion processes or can be formed when large hydrocarbon molecules react with oxidants in the atmosphere and form chemicals that condense onto particles. Sulfate particles are formed via a series of reactions that convert sulfur dioxide, SO_2, which is released into the atmosphere by the combustion of sulfur containing fuels, into sulfuric acid. Nitrate particles are formed via reactions that convert oxides of nitrogen, which are released into the atmosphere by combustion processes, into nitric acid. If particles containing sulfuric acid, nitric acid, and/or organic com-

HYDROGEN ION CONCENTRATION AS pH FROM MEASUREMENTS MADE AT THE FIELD LABORATORIES, 2001



Sites not pictured:

AK03	5.1
HI99	4.6
VI01	5.3

SOURCE: National Atmospheric Deposition Program/National Trends Network. <http://nadp.sws.uiuc.edu>

Figure 1. Spatial distribution of acid deposition.

pounds retain their acidity and are washed out of the atmosphere by rainfall, the rainfall becomes **acid rain**. Figure 1 shows acidity of rainfall averages in the United States and provides a sense of the continental scale of particulate matter air pollution.

The continental and global scale of air pollution problems is not limited to particulate matter. Emissions of greenhouse gases cause global climate change. The presence in the **stratosphere** of ozone-depleting compounds has created polar ozone holes. Atmospheric releases caused by volcanic eruptions and fires have global effects. Atmospheric particles also influence climate and rainfall. The challenges of reducing air pollution call for a sophisticated understanding of atmospheric chemistry, applied at local, regional, continental, and global scales. SEE ALSO ATMOSPHERIC CHEMISTRY.

David T. Allen

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

stratosphere: layer of the atmosphere where ozone is found; starts about 10 km (6.2 mi) above ground

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Alchemy

The alchemical period corresponds to the span of human history that preceded the era in which fundamental understanding in the chemical sciences began to be acquired by humankind. Most scholars believe that alchemy had its roots in ancient Egypt. China has also emerged as a possible source of alchemical thought. Thus, alchemy was the practice of chemistry such as it existed over the approximately twenty-five centuries before the time of Robert Boyle (1627–1697) and Antoine Lavoisier (1743–1784), when chemistry began to develop into the science we know today. Alchemy was an early precursor to science and included many of the chemistry-related processes that have become known as the chemical arts—the working of **metals** and **alloys**, glassmaking and glass coloring, and the preparation and use of pigments, dyes, and therapeutic agents.

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

In its broadest aspect, alchemy appears as a system of philosophy that strove to penetrate the mystery of life as well as to master the formation of inanimate substances. The main goals of the alchemists were the transmutation of base metals into gold and the attainment of the "Philosopher's Stone," a substance that would bring perfection to life. Other embodiments of the Philosopher's Stone were the Elixir Vitae, the Grand Magisterium, and the Red Tincture, all regarded as universal medicines. The alchemical fascination with gold emerged from the idea that gold was the perfect metal. If one could understand the essence of this perfect metal (the theory went), the essence of all substances less perfect than gold could then be understood, which, accordingly, could lead to the creation of all substances, including gold. The Philosopher's Stone incorporated the promise that the perfection of gold could somehow be transferred to life's processes. The Philosopher's Stone was the agent by which base metals could be changed to gold and, by extrapolation, could lead to greater longevity. The Chinese alchemists included these ideas in their approach to alchemistry. They sought the preparation of a liquid form of gold that would promote longevity; liquid gold would contain the essence of the Philosopher's Stone and the search for liquid gold was one route to the Philosopher's Stone. The Chinese alchemists were interested in the preparation of artificial cinnabar, which they believed to be the "life-giving" red pigment that could be used in goldmaking. They were also interested in the transmutation of base metals into gold. Thus, the focus of alchemical thought and process was the manipulation of matter in such a way as to, ultimately, increase longevity.

It is not surprising that in the early days of alchemy, much of the ancient Egyptian expertise in gold refining and goldworking as well as the Egyptian skill with respect to enamelware, the production of colored glass, and the preparation and use of pigments were highly valued by alchemists. In a sense, those Egyptian craftsmen were the first alchemists, even though

The alchemy laboratory in Powder Tower, Prague, which was used circa 1585 by John Dee and Edward Kelley.

they may not have had the same ultimate focus as the practitioners of the alchemical arts.

In the course of the evolution of the alchemical arts, the fundamental properties of matter came under consideration. Aristotle taught that all matter consisted of four fundamental constituent factors or elements—air, water, earth, and fire. All matter was supposed to incorporate these four elements in different combinations and proportions. The changes that a substance could be made to undergo, for example, the burning of wood or the boiling of water, corresponded to a change or changes in the proportions of these four elements within that substance. Thus, alchemy ultimately gave rise to modern chemical thought and, gradually, the goals of alchemy were abandoned. In a broad sense, alchemy can be regarded as a prelude to the chemistry we know today. SEE ALSO AL-RAZI, ABU-BAKR MUHAMMED IBN ZAKARIYA; BOYLE, ROBERT; LAVOISIER, ANTOINE; PARACELSUS.

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Alkali Metals

Alkali metals are the six elements that comprise Group I in the Periodic Table: lithium (Li), sodium (Na), potassium (K), rubidium (Rb), cesium (Cs), and francium (Fr). Especially when dissolved in water, these elements form strong bases (alkalis) capable of reacting with and neutralizing strong acids.

inert: incapable of reacting with another substance

Each metal has the electron configuration of an **inert** (noble) gas plus one electron in the next higher *s* orbital. Thus, Na is $1s^2 2s^2 2p^6 3s^1$ or alternatively (Ne)$3s^1$. Virtually all alkali metal compounds are ionic in nature because this outermost single electron is readily lost, forming relatively stable monovalent ions.

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

Sodium and potassium are abundant in Earth's crust, each comprising about 2.5 percent, and the two being the 6th and 7th most abundant elements, respectively. Other alkali metals are at least one hundred times less abundant. Francium is virtually nonexistent in the environment since all **isotopes** are radioactive with short half-lives.

halogen: element in the periodic family numbered VIIA (or 17 in the modern nomenclature) that includes fluorine, chlorine, bromine, iodine, and astatine

Alkali metals are very reactive, and thus none occurs in a free state in the environment. They spontaneously react with oxygen, water, **halogens**, phosphorus, sulfur, and other substances; lithium even reacts with nitrogen. Reactions with water can be violent, with the evolution of hydrogen gas and formation of strongly alkaline solutions.

potash: the compound potassium oxide, K_2O

Compounds of various alkali metals were known in ancient times, but the great English chemist Sir Humphry Davy first isolated pure metals, purifying potassium and then sodium in 1807. Sodium is derived from "soda," a term used in the Middle Ages to characterize all alkalis, originally from the Latin *sodanum*, which was a headache remedy; its symbol Na is derived from the Latin word for soda, *natrium.* Potassium comes from the French word *potasse* (later the English **potash**), the residue produced when wood ash solutions are evaporated (so-called pot ashes); its symbol K derives from the Latin *kalium* and ultimately Arabic *qali*, meaning "alkali." The Swedish chemist J. A. Arfedson discovered lithium during his analysis of the mineral petalite in 1817, although W. T. Brande and Davy first produced the pure metal. The name is derived from the Greek word *lithos* (meaning "stony").

spectral line: line in a spectrum representing radiation of a single wavelength

During their flame spectrometry experiments on mineral waters in 1860, the German chemists Gustav Kirchhoff and Robert Bunsen determined the existence of cesium from the characteristic two blue lines in the spectrum. Likewise, extracts of the mineral lepidolite exhibited two dark red **spectral lines** from which the presence of Rb was inferred. Thus, cesium derives from the Latin *caesius*, meaning "heavenly blue," whereas rubidium derives from *rubidus*, the Latin word used to describe a very dark red color. Bunsen was able to isolate pure Rb but not Cs, later purified by C. Setterberg.

Since all isotopes of Fr are radioactive, it was not discovered until 1939 at the Curie Institute in Paris by Marguerite Perey, although the Russian chemist Dimitri Mendeleev predicted its existence. Its name derives from that of France, the country where it was discovered.

Because of their metallic and alkaline properties, potassium and especially sodium are widely used in a variety of industrial processes both as metals and as compounds with various other elements. Lithium is rarely used, but does find application in lightweight **alloys** with magnesium. Rubidium and cesium are not commonly utilized industrially, except for some applications in electronics. Sodium and potassium are essential for life, sodium being the principal extracellular and potassium the major intracellular monovalent cations. The other alkali metals have no essential biological role. SEE ALSO Bunsen, Robert; Cesium; Davy, Humphry; Francium; Lithium; Mendeleev, Dimitri; Potassium; Rubidium; Sodium.

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

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Alkaline Earth Metals

Alkaline earth metals are the six elements forming Group IIa in the Periodic Table: beryllium (Be), magnesium (Mg), Calcium (Ca), Barium (Ba), Strontium (Sr), and Radium (Ra)✷. Their oxides are basic (alkaline), especially when combined with water. “Earth” is a historical term applied to nonmetallic substances that are insoluble in water and stable to heating, and also the properties of the oxides. Hence, the term “alkali earths” is often used to describe these elements.

✷See Periodic Table in the For Your Reference section of Volume 1.

Each metal has the electron configuration of an **inert** (noble) gas plus two electrons in the next higher *s* orbital. Thus, Mg is $1s^2 2s^2 2p^6 3s^2$ or alternatively (Ne)$3s^2$. The bonds of most compounds of alkali earths are ionic in nature because these outermost electrons are readily lost, forming stable divalent cations. Mg, however, can form compounds with both ionic and **covalent bonds**, whereas most compounds of Be are covalent. The heavier alkali earths are sometimes compared to Group IIb elements (zinc [Zn], cadmium [Cd], mercury [Hg]) that also have a filled s orbital ($5s^2$), but the filled $4d^{10}$ orbitals and higher **ionization** energies of the latter make compounds of Group IIb elements markedly less ionic in character than those of alkali earths.

inert: incapable of reacting with another substance

covalent bond: bond formed between two atoms that mutually share a pair of electrons

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

Mg and Ca are the eighth and sixth most abundant elements in Earth’s crust at 2.5 and 3.6 percent, respectively. Be, Sr, and Ba comprise 0.001, 0.025, and 0.05 percent, respectively. Ra is radioactive, and since its longest-lived **isotope** ^{226}Ra has a half-life of 1,600 years, there is very little Ra in Earth’s crust. It is nonetheless present because ^{226}Ra is continuously formed by the decay of uranium (^{238}U). Alkali earth elements are

isotope: form of an atom that differs by the number of neutrons in the nucleus very reactive and strongly reducing in character; thus, none occurs in a free state in the environment. They readily react with oxygen, and the pure metals tarnish in air, forming a surface layer of the oxide. The metals are soluble in liquid ammonia, forming covalent compounds with the general formula $M(NH_3)_6$. These solutions are strongly basic and frequently find application in industry.

Oxides of alkali earths were known in ancient times, calcium oxide being lime (from the Latin word *calx*). Magnesium oxide or magnesia was also known, its name probably deriving from a district in Asia Minor. Oxides of the other alkali earths were identified in the eighteenth century. Barium oxide or baryta was found in the mineral called heavy spar and given the name *barys* (from the Greek, meaning "heavy"). Strontia or strontianite (strontium carbonate) was found in a lead mine at Strontian in Scotland. Beryllium oxide was extracted from the mineral beryl (from the Greek word *bèryllos*). Be was originally called glucina (from the Greek *glykys*, meaning "sweet") because of its taste and is sometimes still referred to as *glucinum* in France.

The English chemist Sir Humphry Davy first isolated Mg, Ca, Sr, and Ba in 1808 by means of electrolysis. (Mg was originally called magnium since Davy had already applied the word "magnesium" to the element manganese.) Be was initially isolated from beryl by the French chemist Antoine Bussy and independently in Germany by Friedrich Wöhler in 1828. The discovery of Ra did not occur until 1898 when Marie and Pierre Curie purified it from barium using its radioactivity. They named it from the Latin word *radius* (meaning "ray") because the strength of its radioactivity was more than a million times that of uranium.

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

Because of their metallic properties and low mass, Be and Mg are used to form lightweight **alloys** for structural purposes. Ca sees less industrial use, although the phosphate is sometimes utilized in fertilizers. Sr and Ba have no significant industrial applications. Both Be and Ra are used in various devices, the former because it is quite transparent to x-rays and the latter because it is a ready source of both α- and γ-radiation. Mg and Ca are essential to all living systems for many reasons; the other alkali earths have no known biological roles. SEE ALSO BERYLLIUM; CESIUM; CURIE, MARIE SKLODOWSKA; DAVY, HUMPHRY; FRANCIUM; MAGNESIUM; POTASSIUM; RUBIDIUM; WÖHLER, FRIEDRICH.

Michael E. Maguire

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Allosteric Enzymes

Enzymes are biological catalysts. They accelerate the rates of reactions in cells without being changed themselves during the process of reaction. Allosteric enzymes are a subset of enzymes that are involved in the control and regulation of biological processes. The control of processes is essential to biological systems: A cell that divides out of control has undergone a kind of transformation (cancerous or precancerous) that can threaten an entire organism. There are many processes occurring inside the cell at any one time, and they must coexist in proper balance. This balance is where allosteric enzymes come into play.

Allosteric enzymes have the ability to respond to several different conditions in their environments. Every enzyme contains an active site, the location on the enzyme where it catalyzes its specific reaction. Allosteric enzymes contain a second type of site, called an allosteric site. The allosteric site, through its binding of a nonsubstrate molecule, influences (enhances or impairs) the activity of the enzyme. The word "allosteric" is derived from two Greek words: *allos*, meaning other, and *stereos*, meaning site. Another important feature of allosteric enzymes is that they consist of multiple **polypeptide** chains, with multiple active and allosteric sites.

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

Whereas substrates bind to the active sites of enzymes, other nonsubstrate molecules (allosteric modulators) bind to the allosteric sites. The significance and role of the allosteric site is well illustrated by the example of the enzyme aspartate transcarbamoylase, which catalyzes reaction 1.

$$\text{Aspartate} + \text{Carbamoyl Phosphate} \xrightarrow[\text{transcarbamoylase}]{\text{Aspartate}} \text{N-Carbamoylaspartate} \quad (1)$$

This is the first step of the pathway that leads to the formation of **cytosine**, a building block for **DNA synthesis**. The form of cytosine that is used to synthesize DNA (and **RNA**) is the molecule cytidine triphosphate (CTP). When intracellular CTP concentrations are high, CTP molecules bind more often to the allosteric sites on aspartate transcarbamoylase molecules, causing a change in the shape of the enzyme that slows reaction 1 down markedly. Thus, CTP is an allosteric inhibitor of this enzyme.

There are times in the life of a cell when it needs to make more N-carbamoylaspartate (and eventually more CTP), even when concentrations of CTP are high to begin with. This is particularly true just prior to cell division, because the cell is at this point rapidly synthesizing DNA. Under these conditions, a high concentration of **adenosine triphosphate (ATP)**, another building block of DNA, will be present in the cell. ATP can also bind to the allosteric site on aspartate transcarbamoylase, but, unlike CTP, it acts as an enzyme activator, overcoming the **inhibitory** effect of CTP and thereby leading to the synthesis of more CTP, when CTP concentrations are already high. SEE ALSO ENZYMES; INHIBITORS; PROTEINS.

Paul A. Craig

cytosine: heterocyclic, pyrimidine, amine base found in DNA

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

synthesis: combination of starting materials to form a desired product

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

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

inhibitory: relating to the prevention of an action that would normally occur

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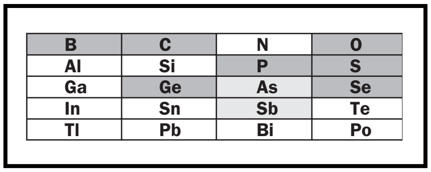

B	C	N	O
Al	Si	P	S
Ga	Ge	As	Se
In	Sn	Sb	Te
Tl	Pb	Bi	Po

Figure 1. Elements that exist as allotropes.

Allotropes

Allotropes are different forms of the same element. Different bonding arrangements between atoms result in different structures with different chemical and physical properties. Allotropes occur only with certain elements, in Groups 13 through 16 in the Periodic Table. This distribution of allotropic elements is illustrated in Figure 1.

Group 13

Boron (B), the second hardest element, is the only allotropic element in Group 13. It is second only to carbon (C) in its ability to form element-element bonded networks. Thus, in addition to amorphous boron, several different allotropes of boron are known, of which three are well characterized. These are red crystalline α-rhombohedral boron, black crystalline β-rhombohedral boron (the most thermodynamically stable allotrope), and black crystalline β-tetragonal boron. All are polymeric and are based on various modes of condensation of the B_{12} icosahedron (Figure 2).

Group 14

In Group 14, only carbon and tin exist as allotropes under normal conditions. For most of recorded history, the only known allotropes of carbon were diamond and graphite. Both are polymeric solids. Diamond forms hard, clear, colorless crystals, and was the first element to have its structure determined by x-ray diffraction. It has the highest **melting point** and is the hardest of the naturally occurring solids. Graphite, the most thermodynamically stable form of carbon, is a dark gray, waxy solid, used extensively as a lubricant. It also comprises the "lead" in pencils.

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

The diamond **lattice** (Figure 3a) contains tetrahedral carbon atoms in an infinite three-dimensional network. Graphite is also an infinite three-dimensional network, but it is made up of planar offset layers of trigonal carbons forming fused hexagonal rings (Figure 3b). The C-C bonds within

lattice: systematic geometrical arrangement of atomic-sized units that constitute the structure of a solid

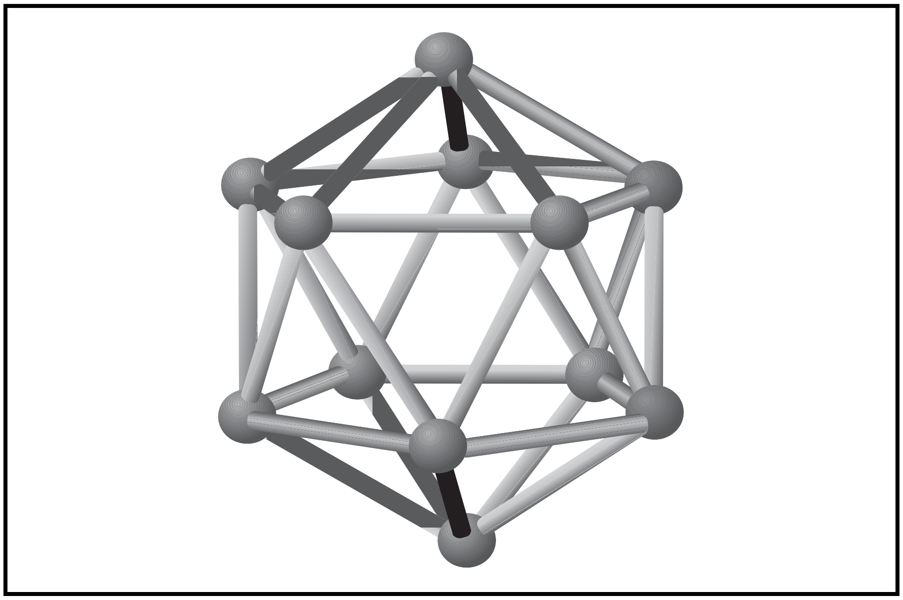

Figure 2. B_{12} icosahedron.

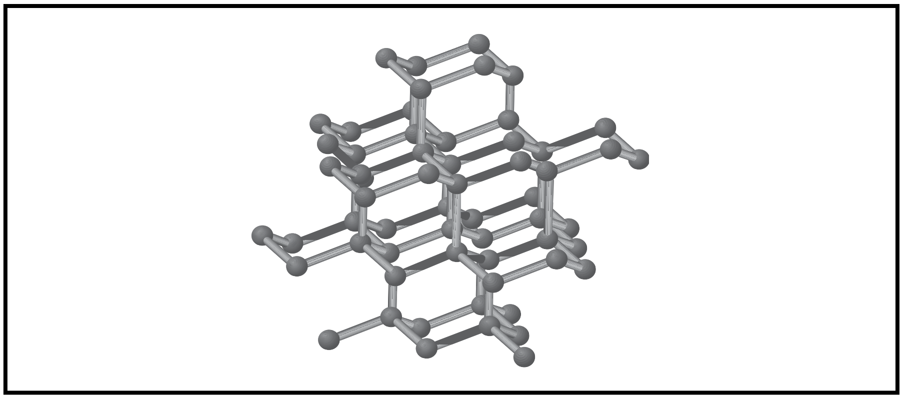

Figure 3a. Portion of the structure of diamond. This structure repeats infinitely in all directions.

a layer are shorter than those of diamond, and are much shorter than the separation between the graphite layers. The weak, nonbonding, interaction between the layers, allowing them to easily slide over each other, accounts for the lubricating properties of graphite.

Diamond and graphite are nonmolecular allotropes of carbon. A range of molecular allotropes of carbon (the fullerenes) has been known since the discovery in 1985 of C_{60} (Figure 4). The sixty carbon atoms approximate a sphere of condensed five- and six-membered rings. Although initially found in the laboratory, fullerenes have since been shown to occur in nature at low concentrations. C_{60} and C_{70} are generally the most abundant and readily isolated fullerenes.

In 1991 carbon nanotubes were discovered. They are more flexible and stronger than commercially available carbon fibers, and can be conductors or semiconductors. Although the mechanism of their formation has not been determined, they can be thought of as the result of "rolling up" a section of a graphite sheet and capping the ends with a hemisphere of C_{60}, C_{70}, or another molecular allotrope fragment. Five- or seven-membered rings can be incorporated among the six-membered rings, leading to an almost infinite range of helical, toroidal, and corkscrew-shaped tubes, all with different mechanical strengths and conductivities.

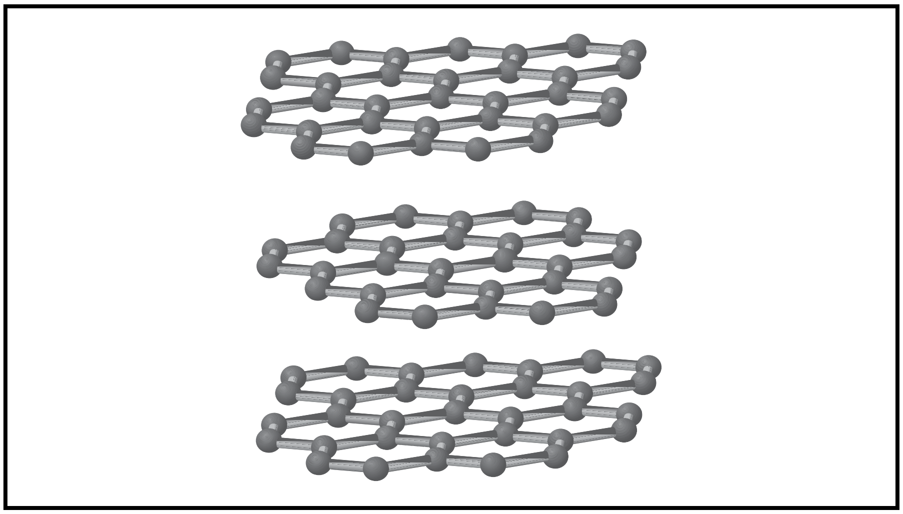

Figure 3b. Portion of the structure of graphite. This structure repeats infinitely in all directions.

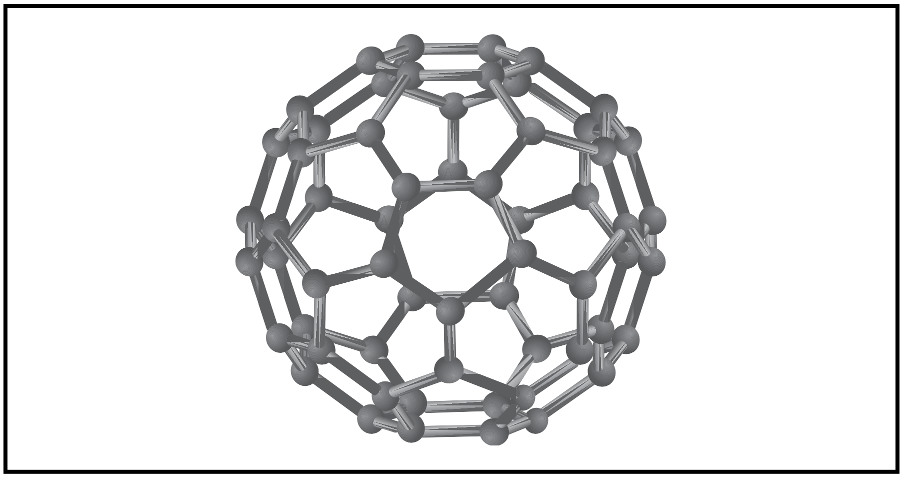

Figure 4. A fullerene allotrope of C_{60}.

Tin is a relatively low melting (232°C) material that exists in two allotropic forms at room temperature and pressure, α-Sn (gray tin) and β-Sn (white tin). α-Sn is the stable form below 13°C and has the diamond structure (Figure 3a). White, or β-Sn is metallic and has a distorted close-packed lattice.

Group 15

arsenic: toxic element of the phosphorus group

volatile: low boiling, readily vaporized

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

There are two allotropic elements in Group 15, phosphorus and **arsenic**. Phosphorus exists in several allotropic forms. The main ones (and those from which the others are derived) are white, red, and black (the thermodynamically stable form at room temperature). Only white and red phosphorus are of industrial importance. Phosphorus was first produced as the common white phosphorus, which is the most **volatile**, most reactive, and most toxic, but the least thermodynamically stable form of phosphorus, α-P_4. It coverts to a polymorphic form, β-P_4, at −76.9°C. White phosphorus is a waxy, nonconductor and reacts with air—the phosphorescent reaction of oxygen with the vapor above the solid producing the yellow-green chemiluminescent light, which gives phosphorus its name (after the Greek god, Eosphoros, the morning star, the bringer of light). The phosphorus in commercial use is amorphous red phosphorus, produced by heating white phosphorus in the absence of air at about 300°C. It melts around 600°C and was long thought to contain polymers formed by breaking a P-P bond of each P_4 tetrahedron of white phosphorus then linking the "opened" tetrahedra (Figures 5a and 5b).

A variety of crystalline modifications (tetragonal red, triclinic red, cubic red), possibly with similar polymeric structures can also be prepared by heating amorphous red phosphorus at over 500°C.

The most thermodynamically stable, and least reactive, form of phosphorus is black phosphorus, which exists as three crystalline (orthorhombic-, rhombohedral- and metallic, or cubic, and one amorphous, allotrope. All are polymeric solids and are practically nonflammable. Both orthorhombic and rhombohedral phosphorus appear black and graphitic, consistent with their layered structures.

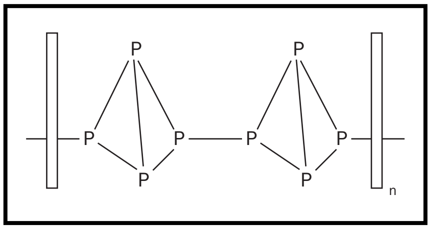

Figure 5a. Linkage of P_4 units in red phosphorus.

A violet crystalline allotrope, **monoclinic** phosphorus, or Hittorf's phosphorus, after its discoverer, can be produced by a complicated thermal and electrolytic procedure. The structure is very complex, consisting of tubes of

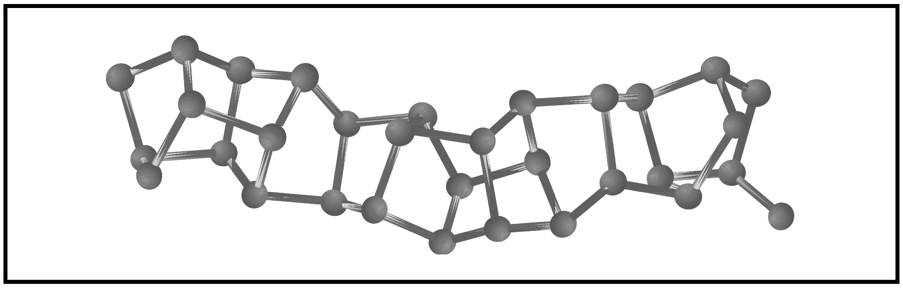

Figure 5(b). Linkage of P_4 units in red phosphorus.

pentagonal cross section joined in pairs to form double layers, which are repeated through the crystal. The tubes are formed from cagelike P_8 and P_9 groups, linked by P_2 units.

At least six forms of solid arsenic have been reported, of which three are amorphous. The most stable and most common form of arsenic at room temperature is a brittle, steel-gray solid (α-As) with a structure analogous to that of rhombohedral black phosphorus. Arsenic vapor contains tetrahedral As_4 molecules, which are thought to be present in the yellow unstable arsenic formed by condensation of the vapor. Arsenic occurs naturally as α-As and also as the mineral arsenolamprite, which may have the same structure as orthorhombic black phosphorus.

Group 16

There are only three allotropic elements in Group 16, oxygen, sulfur, and selenium. Only two oxygen allotropes are known—dinuclear “oxygen” (dioxygen, O_2) and trinuclear ozone (O_3) (Figure 6). Both are gases at room temperature and pressure. Dioxygen exists as a diradical (contains two unpaired electrons) and is the only allotrope of any element with unpaired electrons. Liquid and solid dioxygen are both pale blue because the absorption of light excites the molecule to a higher energy (and much more reactive) electronic state in which all electrons are paired (“singlet” oxygen). Gaseous dioxygen is probably also blue, but the low concentration of the species in the gas phase makes it difficult to observe.

Ozone is a V-shaped, triatomic dark blue gaseous molecule with a bond order of $1\frac{1}{2}$. It is usually prepared from dioxygen by electric discharge (e.g., lightning) and can be detected by its characteristic “sharp” smell—from which it gets its name (after the Greek *ozein*: to smell). Ozone is thermodynamically unstable and reverts spontaneously to dioxygen.

The dark blue color of O_3 is important because it arises from the intense absorption of red and ultraviolet (UV) light. This is the mechanism by which ozone in the atmosphere (the ozone layer) protects Earth from the Sun’s UV radiation. After F_2, ozone is the most powerful oxidant of all the elements.

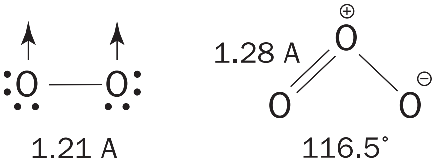

Figure 6. Dioxygen and ozone, the allotropes of oxygen.

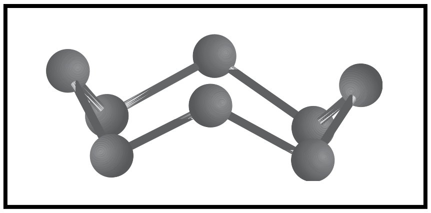

Figure 7. Sulfur allotrope, S_8.

Sulfur (S) is second only to carbon in the number of known allotropes formed. The existence of at least twenty-two sulfur allotropes has been demonstrated. The simplest allotrope of sulfur is the violet disulfur molecule, S_2, analogous to the dioxygen molecule. Unlike O_2, however, S_2 does not occur naturally at room temperature and pressure. It is commonly generated in the vapor generated from sulfur at temperatures above 700°C. It has been detected by the Hubble Space Telescope in volcanic eruptions on Jupiter's satellite, Io.

The most thermodynamically stable of all of the sulfur allotropes and the form in which sulfur ordinarily exists is orthorhombic sulfur, α-S_8, cyclooctasulfur, which contains puckered eight-membered rings, in which each sulfur atom is two-coordinate (Figure 7).

The second allotrope of sulfur to be discovered was cyclohexasulfur (sometimes called rhombohedral sulfur), first reported in 1891. It is the densest of the sulfur allotropes and forms air-sensitive orange-red crystals containing chair-shaped, six-membered rings. Sulfur forms an extensive series of generally yellow crystalline allotropes, S_n (where species with n up to 30 have been identified). The color of liquid sulfur changes from pale yellow to orange, then red and finally to black, near the boiling point (445°C). At about 159°C, the viscosity increases as polymeric sulfur is formed. The liquid is thought to contain chains of sulfur atoms, wound into helices.

Selenium (Se) also exists in several allotropic forms—gray (trigonal) selenium (containing Se_n helical chain polymers), rhombohedral selenium (containing Se_6 molecules), three deep-red monoclinic forms—α-, β-, and γ-selenium (containing Se_8 molecules), amorphous red selenium, and black vitreous selenium, the form in industrial usage. The most thermodynamically stable and the densest form is gray (trigonal) selenium, which contains infinite helical chains of selenium atoms. All other forms revert to gray selenium on warming. In keeping with its density, gray selenium is regarded as metallic, and it is the only form of selenium that conducts electricity. A slight distortion of the helical structure would produce a cubic metallic lattice.

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

The trend from nonmetallic to metallic character upon going down the group is exemplified by the conductivities of these elements. Sulfur is an insulator, selenium and tellurium are semiconductors, while the conductivity of polonium is typical of a true **metal**. In addition, the conductivities of sulfur, selenium, and tellurium increase with increasing temperature, behavior typical of nonmetals, whereas that of polonium increases at lower temperatures, typical of metals. SEE ALSO ARSENIC; BORON; CARBON; FULLERENES; OXYGEN; OZONE; PHOSPHORUS; SELENIUM; SULFUR; TIN.

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Al-Razi, Abu-Bakr Muhammed ibn Zakariya

PERSIAN PHYSICIAN AND ALCHEMIST
ca. 854 C.E.–ca. 930 C.E.

Abu-Bakr Muhammed ibn Zakariya al-Razi (also transliterated as ar-Razi) was born around 854 in Ray, near the city of Teheran (the Persian Empire, now Iran). Al-Razi (in the Latinized West, Rhazes) achieved mastery in a number of fields, including philosophy, logic, poetry, and music. Around the age of thirty he left Ray for Baghdad (now in Iraq), where he was active in the reconstruction of the city hospital. Al-Razi became famous as the most prominent physician in the Islamic world, his fame comparable only to that of another Persian physician, **Ibn Sina** (who became known in the West as Avicenna). Al-Razi's written works in medicine have been widely studied, Latin editions of which remained in use as late as the seventeenth century in Europe. From him we have the earliest distinction between smallpox and measles, and the understanding that smallpox occurs only once in a person's life. As a skilled chemist he recognized the toxicity of **arsenic** (arsenic oxide), but prescribed small doses of this compound in the treatment of many skin diseases and anemia.

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

arsenic: toxic element of the phosphorus group

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

Like his predecessor, the Arabian alchemist Jabir ibn Hayyan (sometimes known as Jabir), al-Razi was influenced in his alchemical views by Aristotle's theory of the four elements. Arabic alchemists had modified the Aristotelian system with respect to the composition of minerals, whereby two elements, mercury and sulfur, were responsible for "the mercurial and sulfurous principles" of a given substance. Later called "philosophical" Mercury and Sulfur, these elements (or principles) were thought to be the substances from which all **metals** were formed. This Sulfur-Mercury theory later became highly influential among European thinkers, for example, Isaac Newton. To this Sulfur and Mercury, al-Razi added a third constituent, a salty principle (which was later reproposed by Paracelsus). In al-Razi's opinion metals were comprised of particles of these elemental constituents, while the identity of the metal depended on the relationships between these indivisible particles and the empty spaces between them.

Persian physician Abu-Bakr Muhammed ibn Zakariya al-Razi.

In contrast to Jabir, who inclined toward numerical mysticism, al-Razi became practiced in experimental work. This is apparent from his two most influential works, *Kitab al-Asrar* (*The Book of Secrets*), and *Kitab sirr al-Asrar* (*The Book of the Secret of Secrets*). In these works he gave several recipes for the alleged transmutation of common metals into precious ones, and crystal or glass into precious stones. Perhaps al-Razi's main contribution to chemistry was his attempt to systematize laboratory practices, to which end he listed contemporary laboratory equipment and techniques used in chemical experiments. Another influential contribution to chemistry was his classification of all the chemical substances he knew, for this is the earliest attempt of which we are aware. Al-Razi divided these substances into four main groups: vegetable, animal, derivative, and mineral. The last group consisted of six subgroups: (1) spirits (**volatile** substances, such as mercury, sulfur, and arsenic sulfide); (2) metals (gold, silver, copper, tin, iron, lead, and "karesin," probably a bronze composed of copper, zinc, and nickel); (3) stones (ores and minerals of iron, copper, zinc, but also glass); (4) atraments (metallic sulfates and their derivatives); (5) boraces (borax, but also sodium carbonate [confused with borax]); and (6) salts (in which categorization sodium chloride appears under four different terms, other salts being sodium carbonate, potassium carbonate, and others).

volatile: low boiling, readily vaporized

In later life al-Razi became blind, which, according to some sources, was a result of his indefatigable activity—for he is said to have written approximately 200 works. According to other sources his blindness was a result of torture, the punishment he was given when he failed to produce precious metals via alchemical transmutation. Al-Razi died in 925 or 935 in Ray. SEE ALSO Newton, Isaac; Paracelsus.

Vladimir Karpenko

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Aluminum

13
Al
ALUMINUM
26.98

MELTING POINT: 660.32°C
BOILING POINT: 2,519°C
DENSITY: 2.70 g/cm^3
MOST COMMON IONS: Al^{3+}

Aluminum is a silvery-white metallic element discovered in 1825 by Danish chemist Hans Christian Ørsted. It is the most abundant **metal** found in Earth's crust, comprising 8.3 percent of the crust's total weight. Its content in seawater, however, is as low as 0.01 gram per metric ton (0.01 part per million). The key **isotope** of aluminum is ^{27}Al with a natural abundance of 100 percent, but seven other isotopes are known, one of which is used as a radioactive tracer (^{26}Al).

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

Aluminum is not found in its metallic state in nature; it is usually found as silicate, oxide, or hydrated oxide (bauxite). Its extraction from ore is difficult and expensive; aluminum is therefore commonly recycled, the energy of recycling being a mere 5 percent of the energy needed to extract the metal.

Aluminum is lightweight, **ductile**, and easily machined. It is protected by an oxide film from reacting with air and water, and is therefore rust-resistant. It is one of the lightest metals but is quite tough and most helpful in **metallurgy**, transportation (e.g., aircraft, automobiles, railroad cars, and boats), and architecture (e.g., window frames and decorative ornaments). It is also used in the manufacture of cooking gear because it is a good conductor of heat. Aluminum foils as thin as 0.18 millimeter (0.007 inch) are a household convenience, protecting food from spoiling and providing insulation. Aluminum-made beverage cans are widely manufactured; more than 100 billion are produced each year. The average human body contains about 35 milligrams (0.0012 ounce) of aluminum, but no known biological role has been established for it; it is, however, suspected to be a factor in the development of Alzheimer's disease. SEE ALSO Electrochemistry.

Jean-Claude Bünzli

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

metallurgy: the science and technology of metals

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Americium

MELTING POINT: **994°C**
BOILING POINT: **2,607°C**
DENSITY: **13.6 g/cm^3**
MOST COMMON IONS: **Am^{3+}, AmO_2^{+}, AmO_2^{2+}**

95
Am
AMERICIUM
243

Americium is a synthetic **radioelement**, first produced in 1944 via the bombardment of plutonium with neutrons by Glenn Seaborg and coworkers as part of the **Manhattan Project**. The first isolation of a compound of americium, $Am(OH)_3$, was achieved by B. B. Cunningham in the fall of 1945. Many radioactive **isotopes** of americium have been isolated and identified, having mass numbers that range from 237 through 247. The longest-lived americium isotope has mass number 243 and a half-life of 7,380 years. The ground state (outer orbital) electronic configuration for a neutral atom is $5f^{2}6d7s^{2}$. The outer *d* and *s* electrons are lost to form americium in its most stable **oxidation** state, +3, in solutions and compounds. Americium is the first of the actinide elements to appear in the characteristic stable trivalent state in solution. Americium, in the V and VI oxidation states, forms the linear oxo cations AmO_2^{+} and AmO_2^{2+}—chemical behavior that is characteristic of actinide elements.

radioelement: a radioactive element; one in which the nucleus spontaneously decomposes (decays) producing α (alpha) and β (beta) particles and gamma rays

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

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

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

Metallic americium has a face-centered cubic structure at its melting point and a double hexagonal closed-packed structure at temperatures below its melting point. The isotope americium-241 emits **α-particles** and γ-rays in its **radioactive decay**, and is a source of γ-radiation, used to measure the thickness of **metals**, coatings, degree of soil compaction, sediment concentration, and so on. The same isotope, mixed with beryllium, is used as a neutron source in oilwell logging and other applications. Americium-241

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

radioactive decay: process involving emission of subatomic particles from the nucleus, typically accompanied by emission of very short wavelength electromagnetic radiation

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

has been used in smoke detectors; its α-emissions ionize the surrounding air and the resulting ions provoke electronic signals when they come into contact with electrodes in the detector. SEE ALSO Actinium; Berkelium; Einsteinium; Fermium; Lawrencium; Mendelevium; Neptunium; Nobelium; Plutonium; Protactinium; Rutherfordium; Seaborg, Glenn Theodore; Uranium.

Gregory R. Choppin

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Amino Acid

In 1953, Harold Urey and Stanley Miller carried out an amazing experiment in which they produced "molecules of life" from a mixture of gases that they proposed existed in a primordial earth. The experiments simulated what would happen when lightning strikes provided energy for chemical reactions in the atmosphere and suggested a hypothesis for how life might have developed on our planet. Amino acids were the vital molecules that formed in this experiment and supported this hypothesis for the origin of life.

An amino acid is a molecule that contains two **functional groups**, an amine and a **carboxylic acid**, as shown in Figure 1. In this illustration there is an additional group called the side chain, designated with an *R.* The variation seen in naturally occurring amino acids arises from differences in this side chain. The twenty naturally occurring molecules are listed in Table 1. In an **aqueous solution**, this structure may change so that a proton from the COOH transfers to the NH_2 and a **zwitterion** is formed. This structure depends on the pH of the solution. Most physiological systems fall into such a pH range so the zwitterion form of amino acids is the most stable form in the human body.

The stereochemistry of amino acids is also an important concept. The carbon atom marked α in Figure 1 is chiral, so an amino acid can be one of two enantiomers. Note that the structure shown in the illustration has the amine group on the right and the **carboxyl group** at the top. This configuration is designated the L form, and all naturally occurring amino acids have this form.

Amino acids are categorized into three groups based on the nature of the side chain. Nine of the amino acids have side chains that are **nonpolar**. Almost 50 percent of the amino acids that are present in proteins have nonpolar side chains. The second category of amino acid contains six different molecules that have polar side chains. Finally, a group of five amino acids have side chains that are not only polar, but charged.

The key chemical characteristic of amino acids is that they link together to form proteins. Because the COOH functional group is an acid and the NH_2 functional group is a base, the two ends of amino acids can readily react with each other. Protein **synthesis** is more complicated than a simple acid-base neutralization, but consider what happens when two amino

functional group: portion of a compound with characteristic atoms acting as a 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 $–CO_2H$ functional group

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

zwitterion: molecule that simultaneously contains a positive and a negative charge

carboxyl group: an organic functional group, –C(O)– found in aldehydes, ketones, and carboxylic acids

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

synthesis: combination of starting materials to form a desired product

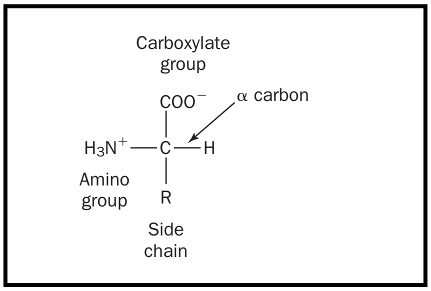

Figure 1.

THE TWENTY COMMON AMINO ACIDS FOUND IN PROTEINS

Name	One-Letter Abbreviation	Three-Letter Abbreviation
Glycine	G	Gly
Alanine	A	Ala
Valine	V	Val
Leucine	L	Leu
Isoleucine	I	Ile
Methionine	M	Met
Phenylalanine	F	Phe
Proline	P	Pro
Serine	S	Ser
Threonine	T	Thr
Cysteine	C	Cys
Asparagine	N	Asn
Glutamine	Q	Gln
Tyrosine	Y	Tyr
Tryptophan	W	Trp
Aspartate	D	Asp
Glutamate	E	Glu
Histidine	H	His
Lysine	K	Lys
Arginine	R	Arg

Table 1. The twenty common amino acids found in proteins.

acids react to form a peptide bond. The new molecule, now a dimer with two amino acid residues still has one end that is an acid and another end that is a base, so it is apparent that the process of forming a peptide bond with another amino acid could be repeated. If many amino acids are strung together, the result is a natural polymer—a protein. SEE ALSO PROTEINS; UREY, HAROLD; ZWITTERION.

Thomas A. Holme

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Analgesic ***See Acetaminophen; Acetylsalicylic Acid.***

Analytical Chemistry

Analytical chemistry is the branch of chemistry that deals with determining the identity and concentration of chemical substances (analytes). G. E. F. Lundell, an American chemist at the National Institute of Standards and Technology likened the questions that analytical chemists answer to the following one: What is the average mass of trout in this stream? To answer this question scientifically, one must devise a way to sample the population of trout in the stream in a representative way, perform the sampling (fishing), get rid of interfering species (e.g., bass, perch, walleye), weigh each trout, record the data, and calculate the average.

Analytical chemistry can be divided into subdisciplines based on the type of samples that are analyzed: atomic, molecular, or biological. Atomic analysis involves the identification and quantification of elements that often occur in complex mixtures. Analytical chemists are often asked to find the

A chemist measures concentrations in a urine sample.

concentration of manganese in a steel sample, for example. Molecular analysis involves the identification and determination of molecules. Analytical chemists are employed to assure that the caffeine concentration in soda is within the limits set by the U.S. Food and Drug Administration (FDA). Recently analytical chemists have worked with biologists to measure concentrations in biological systems. Currently research analytical chemists are working to devise techniques to determine the identity and concentration of all of the proteins in a cell.

What Analytical Chemists Do

Most analyses involve tasks similar to the above trout measurement. Chemists must reproducibly sample a population, remove interfering species, determine the concentration and record the results.

Analytical chemists use a variety of chemical and physical methods to determine identity and concentration. Purely chemical methods were developed in the nineteenth century and therefore are called classical methods. Physical methods involve determinations based on the amount of light absorbed or emitted by the analyte or on the strength of an electrical signal created by the analyte at an electrode.

Classical methods or quantitative analyses include gravimetry, where the amount of a substance is determined by the mass of product generated by a chemical reaction, and titrimetry, where concentration is determined by the volume of a **reagent** needed to completely react with the analyte. These methods are highly accurate and precise but require a sufficient amount of sample, and a concentration of analyte in the sample of at least 0.1 percent. Furthermore these analyses require the constant attention of a trained scientist.

reagent: chemical used to cause a specific chemical reaction

Physical or instrumental methods were extensively developed in the twentieth century and are gradually replacing classical methods. In *Principles of Instrumental Analysis*, three American chemists, Douglas Skoog, F. James Holler, and Timothy Nieman, detail many instrumental methods that use highly complex and often costly machines to determine the identity and concentration of analytes. While these methods often are not as accurate and precise as classical methods, they require much less sample and can determine concentrations much less than 0.1 percent. In fact, Richard Mathies, professor at the University of California at Berkeley, and coworkers recently described methods that can determine the presence of one molecule! In addition, instrumental methods often produce results more rapidly than chemical methods and are the methods of choice when a very large number of samples of the same kind have to be analyzed repetitiously, as in blood analyses.

History

Analytical chemistry began in the late eighteenth century with the work of French chemist Antoine-Laurent Lavoisier and others; the discipline was further developed in the nineteenth century by Carl Fresenius and Karl Friedrich Mohr. As a pharmacist's apprentice in Frankfurt, Germany, Fresenius developed an extensive qualitative analysis scheme that, when it was later published, served as the first textbook of analytical chemistry. He built a laboratory at his house that opened in 1848. Here he trained students in gravimetric techniques that he had developed. Mohr developed laboratory devices such as the pinch clamp burette and the volumetric pipette. He also devised a colorimetric endpoint for silver titrations. It was his 1855 book on titrimetry, *Lehrbuch der Chemisch-Analytischen Titromethode*, that generated widespread interest in the technique.

From Measurement to Concentration

Most modern analytical chemistry techniques are based on instrumental methods involving optical and electrical instruments. Elemental concentrations can be determined by measuring the amount of light absorbed or emitted by gas-phase atoms. Similarly, molecular concentrations are correlated with the emission or absorption of light by molecules in **aqueous solutions**. Electrodes, like the glass pH electrode, measure the electrical potential due to the presence of specific ions in solution. Finally, **chromatographic** methods separate the components of complex mixtures to determine the concentration of each component.

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

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 extent to which the components are absorbed by the stationary phase

Application

One application of instrumental methods is the determination of what drugs a person has taken twenty-four hours after the person took them. In a procedure detailed by Thomas P. Moyer at the Mayo Clinic, a 5-milliliter (0.17-ounce) sample of the patient's blood is analyzed by a technique called high performance liquid chromatography. The sample is treated and injected into a stream of water and methanol that is called a mobile phase. The mobile phase is pumped through a column of fine sand, where the particles of sand have been coated with a thin layer of an oil-like substance (octadecane). The molecules from the blood sample, including the drug, will spend part of their time adsorbed to the modified sand (stationary phase) and part of their time in the mobile phase. The molecules that spend the majority of their time in the mobile phase will it make through the column first.

perpendicular: condition in which two lines (or linear entities like chemical bonds) intersect at a 90-degree angle

To determine when the molecules have exited the column, an ultraviolet (UV) light is placed so that it is **perpendicular** to the flowing stream of mobile phase. The molecules in the blood sample will absorb the UV light and create a signal at the detector. The height of the signal will be proportional to the concentration of the drug in the urine. The time between the sample injection and passage through the column is reproducible and, by comparing it to the time observed when standard samples are used, permits component identification.

Recent Developments

Research is under way to develop techniques that can determine the presence of one atom or molecule in solution, to reduce the size of the instrumentation required, and to analyze the contents of a single cell. These new techniques hopefully will enable the early detection of disease, the remote sensing of a chemical spill, or the rapid analysis of water and air on space vehicles. SEE ALSO Lavoisier, Antoine; Measurement; Solution Chemistry.

G. Brent Dawson

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Androgen ***See Testosterone.***

Anfinsen, Christian

AMERICAN CHEMIST
1916–1995

Christian Boehmer Anfinsen was born in Monessen, Pennsylvania, on March 26, 1916. He earned a B.A. from Swarthmore College in 1937 and an M.S. from the University of Pennsylvania in 1939. In 1943 he received a Ph.D. in biochemistry from Harvard Medical School. He remained at Harvard for seven more years as an instructor and assistant professor of biological chemistry. In 1950 Anfinsen assumed the position of director of the Laboratory of Cellular Physiology and **Metabolism** at the National Heart Institute of the National Institutes of Health (NIH). This move led to a period of thirty years when he split his time between Harvard and the NIH until his retirement in 1981.

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)

Anfinsen began his work on the relationship between protein structure and enzyme function in the mid-1950s in collaboration with F. H. White and Michael Sela at the Weizmann Institute in Rehovot, Israel. This research on the enzyme ribonuclease led him to propose that the structure of the amino acids in sequence along the protein chain contains the information determining the tertiary structure of the enzyme. Anfinsen demonstrated that the denaturation of the enzyme was reversible. After the cleavage of **disulfide bonds** and disruption of tertiary structure, some proteins spontaneously refold to native forms and their function returns. Anfinsen's advanced explanations of this observation became widely accepted.

disulfide bond: bond in a complex substance that involves two bonding sulfur atoms, –S–S–

The pursuit of the tertiary protein structural problem led Anfinsen to the discovery of a microsomal enzyme that catalyzes sulfhydryl-disulfide interchange and accelerates the refolding of denatured proteins which contain disulfide bonds **in vitro**. The kinetics of this folding accounts for the rate of folding of newly synthesized proteins **in vivo**. It was shown, however, that the renaturation required very dilute solutions in many cases to avoid aggregation of the protein in place of proper folding.

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

The importance of Anfinsen's work and that of his followers is the impact it has had on understanding certain diseases that involve the folding of enzymes. Recent discoveries indicate that Alzheimer's disease, cystic fibrosis, mad cow disease, genetic emphysema, and some cancers are all based on some aspect of protein folding gone awry. These folding problems also cause difficulties with the proper naturation of synthetic proteins under development for use as pharmaceuticals. Although Anfinsen could not have known the importance of his discoveries in the 1960s, he was somewhat concerned that the breaking of the genetic **code** and discovery of the α-**helix** structure of **DNA** overshadowed the work on protein and enzyme structure and function. He was awarded the Nobel Prize in chemistry (along with American chemists Stanford Moore and William Howard Stein) in 1972 for his pioneering work on the structure of enzymes and the relationship between the **amino acid sequence** and enzyme function. Anfinsen died in 1995 at the age of seventy-nine.

code: mechanism to convey information on genes and genetic sequence

helix: form of a spiral or coil such as a corkscrew

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

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

Lawrence H. Brannigan

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Antibiotics

Antibiotics are substances that inhibit the growth of microorganisms (anti-**metabolites**) or their replication (a bacteriostatic effect). They were traditionally obtained by extracting them from **cultures** of microbes. However, most drugs on the market today are **semisynthetic** derivatives of natural

metabolites: products of biological activity that are important in metabolism

culture: living material developed in prepared nutrient media

semisynthetic: produced by synthesis from natural starting materials products. Sulfa drugs, discovered in the 1930s, were the first antimicrobial agents put into clinical use. Unfortunately, many bacteria are not susceptible to **sulfonamides**, and with the outbreak of World War II came the need for other more potent antibacterial agents. The serendipitous discovery of penicillin is, without a doubt, the most celebrated breakthrough in the history of antibiotics. In the late 1920s, while working in a London hospital, Alexander Fleming observed a mold overtaking a culture of staphylococcus bacteria he was growing in his laboratory. He extracted juices from the mold and, in 1929, reported that the extract, which he called penicillin, had antiseptic (anti-infectious) activity. The fungus was subsequently identified as *Penicillium notatum* (now called *Penicillium chrysogenum*). It was not until the 1940s that penicillin was put into clinical use. Howard W. Florey, professor of pathology at Oxford's Sir William Dunn School of Pathology, and Ernst B. Chain are credited with culturing the fungus and producing the first significant quantities of penicillin for treating bacterial infections. In 1945 Fleming, Florey, and Chain received the Nobel Prize in physiology or medicine "for the discovery of penicillin and its curative effect in various infectious diseases."


A bottle of Amoxil, one brand name of semisynthetic penicillin amoxicillin.

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

Extracts from microorganisms are still an important source of antibiotics today. Clinically, antibiotics are described as possessing either broad- or narrow-spectrum activity. Bacteria are classified based on a staining technique developed by Danish microbiologist Hans Christian Gram. The bacterial cell walls of gram-positive bacteria stain blue when treated with either crystal violet or methylene blue, while gram-negative bacteria do not retain the stain and appear red. Broad-spectrum antibiotics are capable of inhibiting both gram-positive and gram-negative bacterial cultures. Gram-positive bacteria have simpler cell walls than gram-negative strains and are susceptible to less toxic, narrow-spectrum antibiotics.

β-Lactam Antibiotics

A variety of penicillins have been produced by the fermentation of *Penicillium chrysogenum* in the presence of different nutrients. Penicillin G (benzylpenicillin; see Figure 1) predominates when the culture medium is rich in phenylacetic acid, whereas the incorporation of phenoxyacetic acid favors penicillin V (phenoxymethylpenicillin). Semisynthetic penicillins, such as ampicillin and amoxicillin, are prepared by replacing the aromatic side chain of biosynthetically derived penicillins with other chemical groups. All penicillins are β-lactam (see Figure 2) antibiotics and have the same mechanism of action: They inhibit bacterial cell wall **biosynthesis**.

biosynthesis: formation of a chemical substance by a living organism

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

Bacterial cell walls differ from mammalian cell walls and are therefore attractive targets for antibiotics. Bacterial cell walls contain β-lactam **receptors**, known as penicillin-binding proteins (PBPs). β-Lactam antibiotics

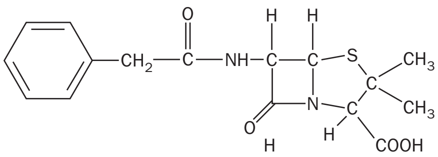


Figure 1. Penicillin G.

bind to the PBPs of bacterial cell walls and prevent their growth and repair. Widespread use of penicillin, however, has led to **drug resistance**. Because microorganisms multiply rapidly, strains of bacteria with enzymes capable of hydrolyzing β-lactam rings (β-lactamases) have evolved. β-lactamases are capable of inactivating β-lactam antibiotics before they bind to receptors on cell walls. As a result, physicians sometimes prescribe β-lactamase inhibitors to patients on penicillin therapy to circumvent drug inactivation by bacterial enzymes.

The cephalosporins comprise another important class of broad-spectrum β-lactam antibiotics. Cephalosporins were originally isolated from cultures of *Cephalosporium acremonium*. Cephalexin (Keflex) is a semisynthetic cephalosporin frequently prescribed to treat ear and skin infections caused by staphylococci or streptococci.

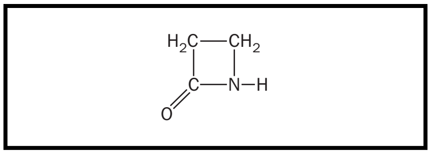


Figure 2. The β-lactam ring.

drug resistance: ability to prevent the action of a particular chemical substance

Antibiotics That Inhibit Protein Synthesis

There are also a large number of antibiotics structurally unrelated to penicillins and cephalosporins. These compounds exert their antimicrobial activity by inhibiting protein biosynthesis. In 1947 chloramphenicol (see Figure 3) was isolated from cultures of *Streptomyces venezuelae.* It is a broad-spectrum bacteriostatic agent that interferes with protein synthesis by binding to bacterial **ribosomes**. The use of chloramphenicol in humans is limited because of the drug's toxicity. It inhibits liver enzymes and suppresses red blood cell formation.

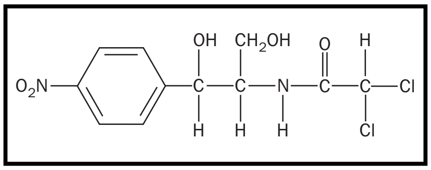


Figure 3. Chloramphenicol.

ribosome: large complex of proteins used to convert amino acids into proteins

streptomycin: antibiotic produced by soil bacteria of genus *Streptomyces*

Aminoglycosides are amino sugars with broad-spectrum antibiotic activity. **Streptomycin**, isolated from *Streptomyces griseus*, was the first aminoglycoside antibiotic discovered. Although streptomycin initially proved to be a potent agent against gram-negative bacteria, rapid microbial resistance to the drug has limited its use and today streptomycin is generally administered in combination with other antibiotics. Neomycin is a broad-spectrum aminoglycoside antibiotic isolated from *Streptomyces fradiae.* However, because of the adverse effects of neomycin on the kidneys and ear, its use in humans is restricted to topical applications, often in combination with other antibiotics or corticosteroids. Concerns over the potential risks associated with aminoglycoside therapy, chiefly nephrotoxicity (kidney disease) and ototoxicity (damage to the ear canal), have diminished their use.

erythromycin: antibiotic used to treat infections

macrolide: substance with a large ring lactone structure

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; a compound with the general formula RC(O)OR′

In 1952 the broad-spectrum antibiotic **erythromycin** was isolated from cultures of *Streptomyces erythreus* (later renamed *Saccharopolyspora erythraea*). The erythromycins are **macrolide** antibiotics that typically have a 12-, 14-, or 16-membered cyclic backbone which is a lactone (a cyclic **ester**; see Figure 4).

Erythromycin A, the major fermentation component of *S. erythraea*, is a 14-membered ring macrolide that is used by medicinal chemists as the foundation for building semisynthetic derivatives of erythromycin antibiotics. (Macrolides inhibit bacteria by interfering with microbial protein biosynthesis.) Semisynthetic macrolides are popular with clinicians because they can be administered orally and have relatively low toxicity. They are often used to treat respiratory tract infections, and have been especially effective against conditions such as Legionnaires' disease and community-acquired pneumonia. Erythromycin therapy is often prescribed for individuals allergic to penicillin. One of the most widely used macrolide antibiotics

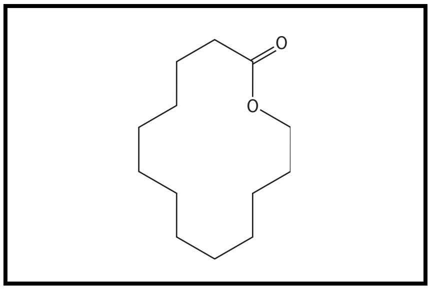
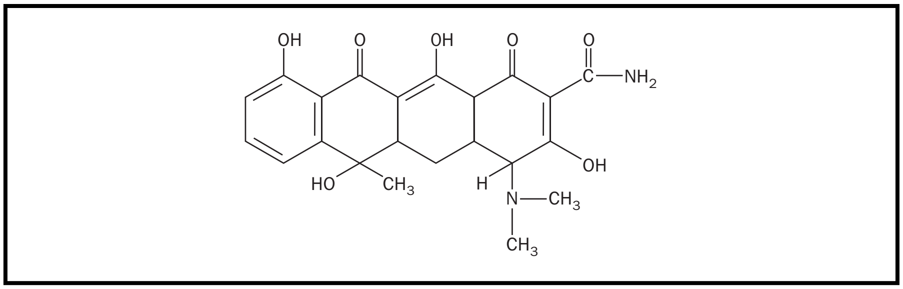


Figure 4. 14-membered lactone.

Figure 5. Tetracycline.



derived from erythromycin A is azithromycin (Zithromax). Resistance to macrolide antibiotics generally involves mutations of bacterial ribosomal **RNA** that prevent macrolide binding.

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

In the late 1940s and early 1950s a series of tetracycline antibiotics was isolated from cultures of streptomyces. All tetracyclines consist of four fused 6-membered rings (see Figure 5). Tetracyclines are broad-spectrum antibiotics that interfere with protein synthesis by binding to bacterial ribosomes. Unfortunately, the frequent use of tetracyclines to treat minor infections has led to resistance among previously susceptible strains of bacteria (pneumococci and staphylococci). Resistance to tetracyclines occurs when bacteria either develop proteins that prevent ribosomal binding by tetracyclines, or synthesize enzymes capable of inactivating tetracyclines.

Widespread use of antibiotics and rapid microbial evolution have led to highly resistant bacterial strains. Although most scientists no longer believe that a single drug will be developed to wipe out all infectious diseases, there is increasing demand for new antimicrobial agents. Currently, combined drug therapy appears to be the most effective means of circumventing microbial resistance to antibiotics. SEE ALSO FLEMING, ALEXANDER; PENICILLIN; SULFA DRUGS.

Nanette M. Wachter

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Anti-inflammatory *See* ***Ibuprofen***.

51
Sb
ANTIMONY
121.75

Antimony

MELTING POINT: **630°C**
BOILING POINT: **1,750°C**
DENSITY: **6.684 g/cm^3**
MOST COMMON IONS: **Sb^{3+}, SbO^+**

Antimony is a **metalloid** element, or a semimetal, its chemical behavior being between those of metals and nonmetals. It is a substance that was known in the ancient world. Antimony sulfide was used as cosmetic eye paint in ancient Egypt, and artifacts composed of almost pure antimony have been found at archaeological sites. Pure antimony is silvery gray and metallic-looking. If antimony is melted and then allowed to crystallize, it manifests a characteristic pattern known as the star of antimony.

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

There are two stable **isotopes** of antimony: ^{121}Sb (57.25%) and ^{123}Sb (42.75%), leading to an **atomic weight** calculation of 121.75. It is not abundant in Earth's crust (an abundance of only 0.2 parts per million), but several antimony compounds occur as minerals, including stibnite, Sb_2S_3, the cosmetic mentioned above. Antimony is also a common impurity in ores of copper, lead, and silver. When antimony is heated in air it burns vigorously, forming the white oxide Sb_2O_3.

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

atomic weight: weight of a single atom of an element in atomic mass units (AMU)

Alloys of antimony and other metals have many applications. Alloys of antimony and lead are much harder than pure lead and are used in the making of low-friction bearings, lead-acid batteries, and printing type metal. Alloys of antimony, lead, and tin have the unusual property of expanding upon **crystallization** from a melt, and thus fill all recesses of the molds used to make printing type. Antimony compounds are used as flame-retardants and in paints, glazes for ceramics, specialty glasses, and semiconductor materials. The sulfide Sb_2S_5 is a rubber additive. Tartar emetic, a complex antimony tartrate of formula $K[C_4H_2O_5Sb(OH)_2] \cdot \frac{1}{2}H_2O$ has been used medically for over three hundred years.

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

crystallization: process of producing crystals of a substance when a saturated solution in an appropriate solvent is either cooled or some solvent is removed by evaporation

Harold Goldwhite

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Antipyretic ***See Acetaminophen.***

Argon

MELTING POINT: −189.3°C
BOILING POINT: −185.8°C
DENSITY: Unknown
MOST COMMON IONS: None known

18
Ar
ARGON
39.948

Argon is an odorless, colorless monatomic gas at room temperature. Although it constitutes about 1 percent of the atmosphere, it was not discovered until 1894, when John William Strutt (Lord Rayleigh) and William Ramsay isolated it from the more reactive components of air. Argon is the most abundant **noble gas** and it was the first to be found. Its discovery prompted confusion over how to fit it into the periodic table: No other **inert**, monatomic gases were then known. Furthermore, its atomic weight placed it between the very reactive **metals** potassium and calcium. Ramsay suggested a new family of elements (the noble gases), and had isolated four additional members by 1898.

noble gas: element characterized by inert nature; located in the rightmost column in the Periodic Table

inert: incapable of reacting with another substance

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

The element takes its name from the Greek *argos*, meaning slow or lazy, because it is extremely unreactive. Indeed, its first stable neutral compound, argon fluorohydride (HArF), was not reported until 2000, and it exists only within a low-temperature solid matrix. Because argon in effect does not form chemical bonds, it is frequently used in the research of nonbonding chemical interactions, such as van der Waals forces and surface adsorption. Inertness makes argon useful in incandescent light bulbs: It protects the hot filament from **oxidation** and slows its evaporation. It is used to generate an inert atmosphere for other chemical reactions in industry and research. Argon is the glowing gas that occupies some fluorescent tubes, and it is an insulating filler in some double-pane thermal windows.

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

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

The principal **isotope** of argon is ^{40}Ar (99.6% abundance); it has two other stable isotopes, ^{36}Ar (0.3%) and ^{38}Ar (0.1%). Argon-40 is formed by β-decay of the long-lived potassium isotope ^{39}K. SEE ALSO NOBLE GASES; RAMSAY, WILLIAM; STRUTT, JOHN.

Carmen Giunta

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Internet Resources

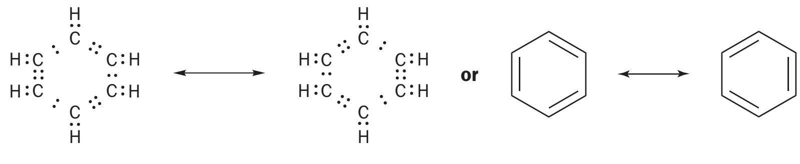
WebElements™ Periodic Table Available from <http://www.webelements.com/>.

Aromaticity

The literal meaning of "aromaticity" is "fragrance," but the word has a special meaning in chemistry. Aromaticity has to do with the unusual stability of the compound benzene and its derivatives, as well as certain other unsaturated ring compounds. The structures of these compounds are often shown to contain double bonds, but they do not actually behave like double bonds. For example, **reagents** such as bromine react with benzene by substitution rather than addition. Benzene and its derivatives had long been referred to as aromatic because of their distinctive odors.

reagent: chemical used to cause a specific chemical reaction

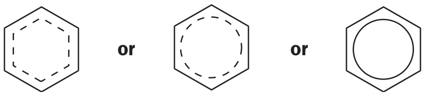
The structure for benzene is often shown as a hybrid of the two Kekulé formulas:



(1)

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

The double-headed "resonance arrow" does not signify an **equilibrium** in which the two structures are very rapidly shifting back and forth (as was once thought to be the case). Instead it means that the actual structure is not like either of the two Kekulé structures but is rather a *resonance hybrid* of the two. (The length of a carbon-carbon single bond is 1.54 Angstroms, and that of a double bond, 1.33 Angstroms. X-ray analysis shows that in benzene all the C-C distances are identical and equal to 1.40 Angstroms.) The C-C bonds in benzene are neither single nor double bonds, but something in between. Perhaps the benzene ring is best represented as follows:



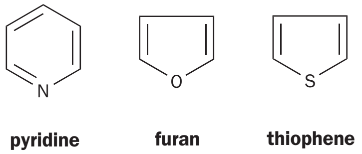
(2)

The simple circle-inscribed hexagon on the right has become a popular alternative to the classical Kekulé structure and is probably the benzene formula most widely used.

The aromaticity of the benzene ring can be assessed by measuring its "resonance energy." One way to do this is by measuring its heat of hydrogenation. When hydrogen is added to a double bond, the heat of reaction is about 120 kilojoules per mole. If benzene really had three double bonds, its heat of hydrogenation should be about 360 kilojoules per mole. In contrast, its actual heat of hydrogenation is only about 210 kilojoules per mole. This is 150 kilojoules per mole less than expected if benzene actually contained three double bonds. The 150 kilojoules per mole is a measure of the extra stability that benzene has because its π electrons are **delocalized**. (The π electrons are those involved in the second bonding pair of the double bond.)

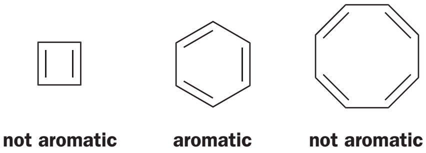
delocalized: of a type of electron that can be shared by more than one orbital or atom

Benzene is not the only compound that exhibits such unusual stability. The following heterocyclic unsaturated ring compounds also exhibit aromatic behavior:



(3)

In 1890 Eugen Bamberger was the first to suggest that six was the magic number of "potential valences" that caused an unsaturated ring to be aromatic. In 1899 Johannes Thiele suggested that any ring that had a completely conjugated set of double bonds around the ring should be aromatic; when cyclobutadiene and cyclooctatetraene were prepared, however, neither turned out to be aromatic.

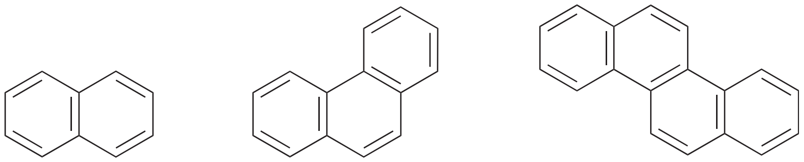


(4)

In the 1920s Armit and Robinson pointed out that it was conjugated ring systems with six multiple bonding electrons that seemed to have special stability. They spoke of an "aromatic sextet" of electrons as being necessary for aromaticity.

Hückel's Rule

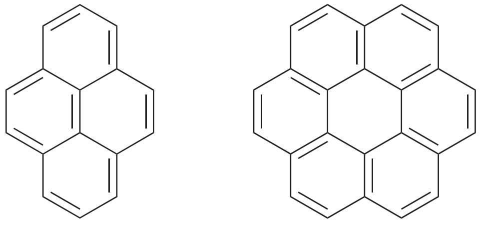
German physicist Erich Hückel used the molecular orbital theory to explain the stability of benzene and other aromatic compounds. Hückel's rule determines the number of π electrons that give stability to an unsaturated planar ring according to the formula $4n + 2$. For benzene and its analogs, n = 1; therefore, 4n + 2 = 6 (the aromatic sextet). The rule was calculated for single ring molecules and does not generally apply to multiring systems. Although many polycyclic aromatic molecules do follow Hückel's rule (Figure 5), some do not (Figure 6). For example, pyrene has sixteen π electrons and coronene has twenty-four, but both are aromatic.


(5)

naphthalene
($n = 2$)
$4n + 2 = 10$

phenanthrene
($n = 3$)
$4n + 2 = 14$

chrysene
($n = 4$)
$4n + 2 = 18$

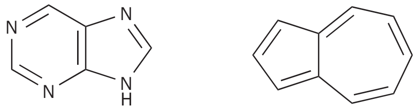

(6)

pyrene **coronene**

The molecules in Figures 5 and 6 all have fused rings (in which some carbon atoms are part of two or more rings). In general, molecules with fused rings tend to be less stable than single aromatic rings.

Aromatic polycyclic compounds need not contain contain benzene rings. For example, purine, which contains two fused heterocyclic rings, is aromatic. Azulene, named for its deep blue color, is also aromatic, although one ring has five carbon atoms and the other has seven. It is not, however, as aromatic as its **isomer** naphthalene, which has two fused benzene rings.

isomer: substance with an identical molecular formula but a different structural formula



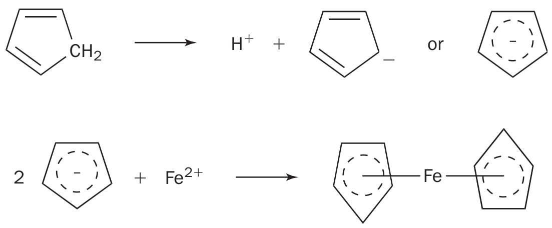
(7)

purine **azulene**

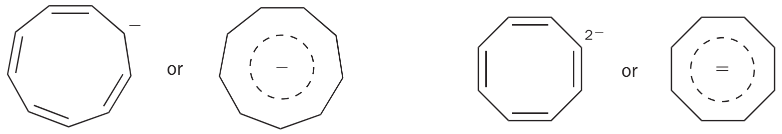
Aromatic Ions

Cyclopentadiene is an acidic hydrocarbon. In 1928 English chemist Christopher Ingold suggested that this was because the cyclopentadienyl **anion** had an aromatic sextet of electrons. This was the first case of aromatic character being attributed to an ion. An interesting derivative made from this very stable carbanion was *ferrocene* (discovered in 1951).

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

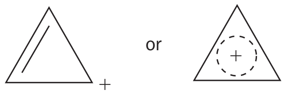


(8)

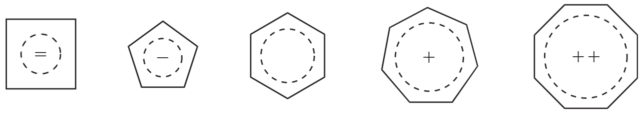


(9)

In 1945 Michael J. S. Dewar suggested that the *tropylium* ion (the cation derived from cycloheptatriene) should also be aromatic (Figure 9). This was confirmed in 1954; since then, the dianion of butadiene and the dication of cyclooctatetraene have also been shown to be aromatic. Like benzene, all four of these ions are planar rings with six π electrons. According to Hückel's rule the cyclopropene cation should also exhibit aromaticity, and it does. (In this case n = 0, and 4n + 2 = 2.) The planar anion of cyclononatetraene and the dianion of cyclooctatetraene should also be aromatic (n = 2, and 4n + 2 = 10), and both of them are.



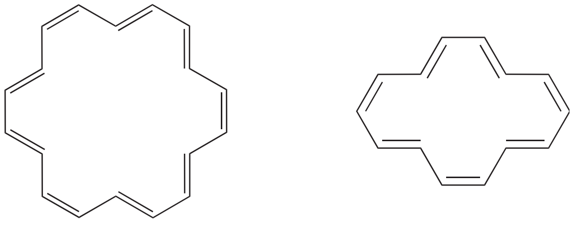
(10)



(11)

Other Nonclassical Aromatic Compounds

Hückel's rule also predicted aromatic stability for certain large ring polyenes called *annulenes.* Fully conjugated [14]-annulene and [18]-annulene do have aromatic properties, especially at lower temperatures (Figure 12), as does [22]-annulene. They contain fourteen, eighteen, and twenty-two π electrons, respectively, corresponding to values of 4n + 2 where n = 3, 4, and 5, and all the molecules are planar. The [12]-, [16]-, [20]-, and [24]-annulenes, on the other hand, do not obey Hückel's rule, and they are not aromatic.



[18] - annulene **[14] - annulene**

(12)

Although aromatic rings are normally planar, with uninterrupted conjugation, that is not always the case. When cyclooctatetraene is treated with acid, the *homotropylium* ion is formed. It has six electrons in a seven-membered ring that has a CH_2 group lying in a **perpendicular** plane, yet is aromatic.

perpendicular: condition in which two lines (or linear entities like chemical bonds) intersect at a 90-degree angle

What Is Aromaticity?

At one time the term "aromatic" applied only to benzene. To some chemists it still simply means "like benzene." An aromatic molecule is a planar ring with a circular cloud of delocalized π electrons. It is an unsaturated cyclic molecule stabilized by resonance. It is a very stable unsaturated ring that reacts by substitution instead of addition. Or, according to Hückel's rule, it is a fully conjugated unsaturated ring that has $4n + 2$ π electrons.

How do you know whether or not a molecule is aromatic? If an unsaturated ring compound is aromatic, its heat of hydrogenation and its heat of **combustion** will both be considerably less than they would be if double bonds were present. Its bond distances (as measured by x-ray or electron diffraction or by microwave **spectroscopy**) will be uniform. It will have longer wavelength absorption bands in the ultraviolet region of the spectrum. An aromatic compound will have **diamagnetic** anisotropy (meaning that a crystal will have more magnetic susceptibility along one axis than the other two). It will also be *diatropic*; in other words, because its π electrons are delocalized, protons attached to the ring will be shifted downfield in the nuclear magnetic resonance (NMR) spectrum from where they would be if double bonds were present. In fact, NMR can be used to measure the degree of aromaticity in a molecule by how well its ring of π electrons can sustain an induced "ring current." SEE ALSO NUCLEAR MAGNETIC RESONANCE.

Doris K. Kolb

combustion: burning, the reaction with oxygen

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

diamagnetic: property of a substance that causes it to be repelled by a magnetic field

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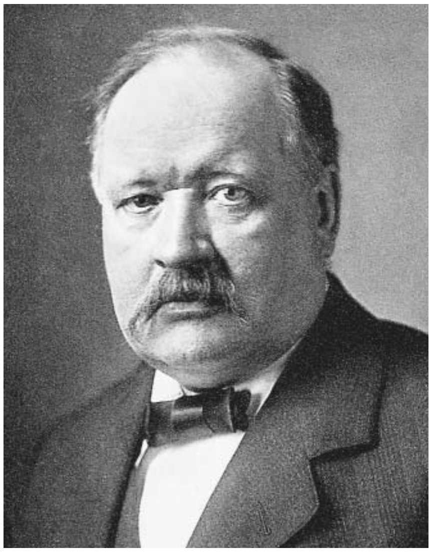
Arrhenius, Svante

COFOUNDER OF MODERN PHYSICAL CHEMISTRY
1859–1927



Swedish chemist Svante August Arrhenius, recipient of the 1903 Nobel Prize in chemistry, "in recognition of the extraordinary services he has rendered to the advancement of chemistry by his electrolytic theory of dissociation."

Svante August Arrhenius, born in Vik, Sweden, is regarded as the cofounder of modern physical chemistry. For his theory of electrolytic dissociation, Arrhenius received the Nobel Prize in chemistry in 1903. He also made important contributions to chemical kinetics and many other branches of science.

In 1884 Arrhenius obtained his Ph.D. from the University of Uppsala with a thesis on the conductivities of electrolytic solutions. Although poorly rated by his examiners, his thesis attracted the attention of the most distinguished physicists and physical chemists in Europe at the time. Arrhenius collaborated with a number of them from 1886 until 1890. Based on his international reputation, he secured a post at the Technical High School in Stockholm, first as a lecturer, then as a professor, and finally as its rector. He later became director of the new physical chemistry institute of the Nobel Foundation in 1905. By that time, his interests had already shifted toward other fields of science.

Arrhenius is mainly known for his equation describing the temperature dependence of chemical reaction rates:

$$k = A \exp(-E/RT)$$

with k being the reaction rate constant, A a preexponential factor, E the activation energy, R the gas constant, and T the absolute temperature. Although the equation was first formulated by Dutch physical chemist Jacobus Hendricus van't Hoff in 1884, Arrhenius provided the interpretation of it that is still in use today. He suggested that the crucial step in a chemical reaction was the formation of activated molecules from the reactant molecules and that both states were in **equilibrium**, separated from each other by the activation energy E. Accordingly, he explained the temperature dependence of the reaction rate as a change of equilibrium, such that with increasing temperature more activated molecules were formed to undergo reaction. Furthermore, plotting the experimental results of ln k against $1/T$ (the so-called Arrhenius plot) yielded in many cases a straight line, from the slope of which one could easily calculate the activation energy E.

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

Arrhenius's most famous contribution, making him with the German physical chemist Friedrich Wilhelm Ostwald and van't Hoff a cofounder of modern physical chemistry, was his theory of electrolytic dissociation. Electrolytes are substances such as salts, acids, and bases that conduct electric current in solutions. Arrhenius suggested that every electrolyte, once dissolved in a solvent like water, dissociated into oppositely charged ions to a certain degree that depended on its nature and overall concentration. Before this explanation, chemists had continued to believe that electrolytes dissolved as uncharged molecules that could be separated only by strong electric forces, such as in electrolysis. Although the forces for electrolytic dissociation remained unclear for some time, Arrhenius's assumption could explain a wide range of phenomena and laws beyond electrochemistry. This included Raoult's laws of vapor pressure lowering and freezing point depression, Ostwald's dilution law, and van't Hoff's law of osmotic pressure of solutions. As Ostwald later showed in his acid-base theory, it also provided a quantitative understanding of the chemical activities of electrolytes in solution.

In his later years, Arrhenius applied the concepts of physical chemistry and physics to many other branches of science, including biochemistry, geo- and cosmic physics, and meteorology. In retrospect, his most remarkable contribution was perhaps his model of the **greenhouse effect**, according to which the temperature of Earth's lower atmosphere is determined by the concentration of carbon dioxide. Earth's surface, after being warmed by sunlight, emits energy in the form of infrared radiation, which is absorbed by molecules in the atmosphere, particularly carbon dioxide; the absorption of infrared radiation leads to heat. At that time, the greenhouse effect model was used to explain the glacial periods, rather than any climatic changes induced by the human production of carbon dioxide, as is the case today. SEE ALSO GLOBAL WARMING; OSTWALD, FRIEDRICH WILHELM; VAN'T HOFF, JACOBUS.

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

Joachim Schummer

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33

As

ARSENIC

74.9216

Arsenic

MELTING POINT: 817°C
BOILING POINT: 613°C
DENSITY: 5.72 g/cm^3
MOST COMMON IONS: As^{3+}, AsO_2^-

Arsenic is the twentieth most abundant element in Earth's crust, averaging a concentration of approximately 2 ppm. Arsenopyrite (FeAsS) is its most common mineral. Arsenic occurs widely in nature, and most abundantly in sulfide ores and the products of volcanic eruptions. Arsenic concentrations in rock and soil are highly variable; the highest concentrations are in hydrothermal sulfide mineralization areas.

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

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

Arsenic has two common **oxidation** states: +5, the predominant one, and the less thermodynamically stable +3. Arsenic has twenty-three **isotopes**; of these, one (mass 75) is stable. The other isotopes have very short half-lives.

Trace amounts of arsenic occur in groundwater; it may cause human cancers at concentrations in drinking water of about 300 ppb. The U.S. Environmental Protection Agency (EPA) has proposed lowering the maximum allowable arsenic concentration in U.S. drinking water from 50 to 5 ppb. The latter lower limit is still controversial.

The properties of arsenic sulfides were known to physicians and "professional poisoners" in the fifth century B.C.E. Albertus Magnus (1193–1280) is credited with having isolated elemental arsenic by heating auripigment (As_2S_3) with soap.

metallurgy: the science and technology of metals

Beneficial effects of arsenic compounds have been known for a very long time. Arsenic was important in the development of **metallurgy** at the beginning of the Bronze Age, and later as a pigment and as an incendiary warfare ingredient. Since ancient and classical times arsenic formulations have been prescribed to cure diseases.

Historically arsenic compounds were alchemical ingredients and the art of secret poisoning was a part of the social and political life of many societies. Arsenic toxicity resulted in the deaths of painters who mixed arsenic pigments.

Between 1850 and 1950 humans were habitually exposed to arsenic in medicine, food, air, and water. Consumer products of the period that contained arsenic included pigments, medicated soaps, embalming solutions, adhesive envelopes, glass, fly-powder, and rat poison.

ferrous: older name for iron in the +2 oxidation state

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

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

smelting: process by which ores are reduced in the production of metals

Currently arsenic is a part of wood preservatives, some pesticides, non**ferrous alloys**, and semiconductor manufacture. Arsenic may be released into the environment from **metal smelting** and coal burning. SEE ALSO TOXICITY.

Jeffrey C. Reid

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"USGS—Minerals Information: Arsenic." U.S. Geological Survey. Available from <http://minerals.usgs.gov/minerals/pubs/commodity/arsenic/>.

Artificial Sweeteners

There are presently four artificial, or synthetic, sweeteners that have been approved by the U.S. Food and Drug Administration (FDA): saccharin, aspartame, acesulfame-K, and sucralose. People use artificial sweeteners because they suffer from diseases such as diabetes mellitus, because they are concerned about dental caries and periodontal disease, or because they wish to lose or to avoid gaining weight. Artificial sweeteners in very small quantities give foods sweetness, and most are not metabolized, meaning that the artificial sweeteners themselves furnish zero dietary calories.

Sweetener Molecules and Sweetness

Sucrose and most artificial sweeteners are chemically quite dissimilar. Sucrose ($C_{12}H_{22}O_{11}$), the most common "natural" sweetener, is a disaccharide composed of the **monosaccharides glucose** and fructose. Saccharin has the formula $C_7H_5O_3NS$. Aspartame ($C_{13}H_{18}O_5N_2$), L-aspartyl-L-phenylalanine methyl **ester**, is the methyl ester of a dipeptide. Acesulfame-K has the formula $C_5H_6O_3NS$. Sucralose ($C_{11}H_{19}O_8Cl_3$) is prepared from sucrose via the substitution of three chloride groups for three hydroxyl groups. The molecular structures of sucrose, saccharin, aspartame, acesulfame-K, and sucralose are shown in Figure 1.

A sweetener must be soluble in water and the molecule must bind readily to a specific kind of **receptor** molecule at the surface of the tongue. The receptor is coupled to a G-protein, which dissociates when the sweetener binds to the receptor, activating a nearby enzyme, and triggering a sequence of events resulting in signals that are carried to and interpreted by the brain. The sweetness "signal" depends on this interaction between receptor and sweetener. The importance of molecular shape to sweetness is illustrated by the case of aspartame, as its stereo **isomer**, L-aspartyl-D-phenylalanine methyl ester, has a bitter, not a sweet, taste.

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

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

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; a compound with the general formula $RC(O)OR^1$

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

isomer: substance with an identical molecular formula but a different structural formula

Discovery, Sweetness, and Metabolic Products

Saccharin was the first artificial sweetener, discovered in 1879 by Constantin Fahlberg at Johns Hopkins University. The Monsanto Chemical Works was incorporated in 1901 to produce saccharin in the United States. Saccharin is easy to make, stable when heated, and is approximately 300 times sweeter than sucrose when equal quantities are compared. One common saccharin product is Sweet and Low.

Saccharin does not accumulate in body tissues. Controversy over the use of saccharin has existed for over a century. In the 1960s and early 1970s saccharin and/or its impurities were shown to cause bladder cancer in rats.

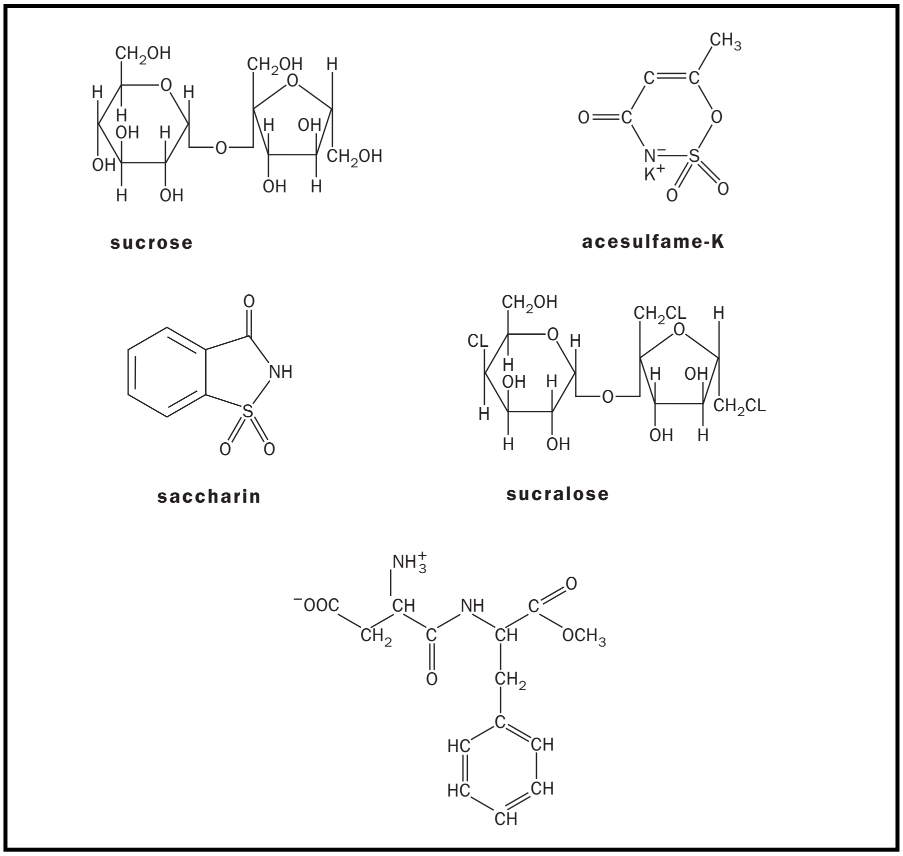

Figure 1. Molecular structures of sucrose and FDA-approved artificial sweetners.

In 1977 a Canadian study concluded that saccharin was the causative agent. Saccharin was banned in Canada. At about the same time the FDA proposed to limit the use of saccharin, but public outcry was so great that the U.S. Congress placed a moratorium on bans of saccharin until further studies were completed. The original moratorium was in effect for two years but has been continually extended to the present day.

Aspartame was discovered in 1965 by James Schlatter at G.D. Searle & Company. Aspartame is relatively easy to make and is approximately 200 times sweeter than sucrose. It is most commonly sold as NutraSweet and Equal. It is less stable than saccharin and breaks down above 29.44°C (85°F). In the body, aspartame is broken down into/absorbed as products that include aspartate, phenylalanine, and methanol. Phenylalanine is toxic to individuals who are homozygous (having identical genes in homologous chromosomes) for phenylketonuria, a genetic disease wherein individuals cannot **catabolize** phenylalanine. Phenylketonuria causes mental retardation. Products containing aspartame must therefore be labeled for phenylalanine. The FDA considers aspartame to be one of the most thoroughly studied and tested food additives and has judged it to be safe. Controversy still lingers with respect to the effects of aspartame's breakdown products—phenylalanine and aspartate, as well as methanol and its breakdown products **formaldehyde** and formate.

catabolism: metabolic process involving breakdown of a molecule into smaller ones resulting in a release of energy

formaldehyde: name given to the simplest aldehyde HC(O)H, and it contains the −C(O)H functional group

Acesulfame-K was discovered in 1967 by scientists working at Hoechst AG. It is also called Sunett. It is approximately 200 times sweeter than sugar. It has a long shelf life and does not break down in foods that are cooked or

Artificial sweeteners, such as those in diet sodas, contain no calories and are used by dieters and diabetics.

baked. Over ninety studies have been completed that have concluded that acesulfame-K is safe.

Sucralose was discovered in 1976 by researchers at Tate & Lyle PLC. It is also called Splenda. Sucralose is approximately 600 times sweeter than sugar and is stable at high temperatures. It was approved by the FDA in 1998–1999, and it is supported by a safety database of more than 110 studies. Concerns persist, including concerns over possible side effects associated with breakdown products (which include chlorine and 1,6-dichlorofructose), shrunken thymus glands (and their impacts on the immune system), and unanticipated effects that may not have manifested during the short time that sucralose has been used. SEE ALSO Toxicity.

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Aspertame *See Artificial Sweetners.*

Aspirin *See Acetylsalicyclic Acid.*

Ascorbic Acid

Ascorbic acid or **vitamin** C is an **antiscorbutic** agent. Scurvy is a disease that potentially ranks as the second most important nutritional deficiency, after protein-calorie malnutrition. Scurvy, once common in among sailors, causes bleeding and inflamed gums, loose teeth, poor wound healing, pain in the joints, muscle wasting, etc. The structure of vitamin C is simple (see Figure 1), resembling a monosaccharide, and most animals are able to synthesize ascorbic acid. Only primates, guinea pigs, and some fruit bats have lost the ability to synthesize it.

Vitamins are organic molecules that mainly function as catalysts for reactions in the body. A **catalyst** is a substance that allows a chemical reaction to occur using less energy and less time than it would take under normal conditions.

Vitamin C is water-soluble and very important to all humans because it is vital to the production of collagen. Inside the cell, it helps form a **precursor molecule** called "procollagen" that is later packaged and modified into collagen outside the cell. Collagen is a gluelike substance that binds cells together to form tissues. It is the most abundant of the fibers contained in connective tissues. Connective tissue gives the human body form and supports its organs.

Vitamin C is also important as it helps protect the fat-soluble vitamins A and E, as well as fatty acids from **oxidation**. It is therefore a **reducing agent** and scavenger of radicals (sink of radicals). Radicals, molecules with unpaired electrons, are very harmful to the body as a result of their high reactivity, which may induce mutations and possibly cancer. Vitamin C, being an excellent source of electrons, can therefore donate electrons to free radicals such as hydroxyl and superoxide and quench their reactivity.

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

antiscorbutic: substance that has an effect on scurvy

catalyst: substance that aids in a reaction while retaining its own chemical identity

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

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

reducing agent: substance that causes reduction, a process during which electrons are lost (or hydrogen atoms gained)

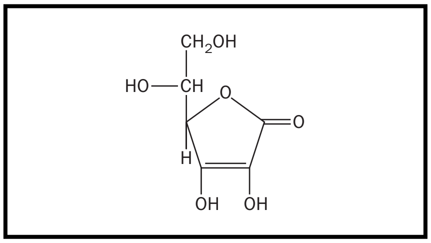

Figure 1. Ascorbic acid (vitamin C).

A debate exists over the anticancer properties of vitamin C. However, current evidence suggests that the major benefit of ascorbic acid with regard to cancer may be in reducing the risk of developing cancer, rather than in therapy. Vitamin C can work inside the cells to protect **DNA** (deoxyribonucleic acid), the hereditary material in cells, from the damage caused by free radicals. Also, it can reduce the development of nitrosamines (amines linked to the NO group) from nitrates, chemicals that are commonly used in processed foods. Once formed, nitrosamine can become carcinogenic (cancer-causing).

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

Sources of vitamin C are numerous: citrus fruits such as oranges, limes, and grapefruits and vegetables including tomatoes, green peppers, potatoes, and many others. The recommended dietary allowance (RDA) of vitamin C is 60 milligrams (0.0021 ounces) per day. An average American ingests about 72 milligrams (0.0025 ounces) a day. Some studies suggest higher daily doses especially for the elderly, women, and the infirm. For example, the late Linus Pauling, best known for his theory on chemical bonding and a two-time Nobel Prize winner, consumed several grams of vitamin C per day for the last forty years of his life and lived to age ninety-three. SEE ALSO Catalysis and Catalysts; Pauling, Linus.

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Astatine

85
At
ASTATINE
210

MELTING POINT: 302°C
BOILING POINT: 337°C
DENSITY: UNKNOWN
MOST COMMON IONS: At^-, AtO^-, AtO_3^-

Astatine is a radioactive halogen (the heaviest of the halogen elements) and is a solid at room temperature. Dale R. Carson, K. R. MacKenzie, and Emilio Segrè of the University of California produced the element in 1940 by bombarding an isotope of bismuth (^{209}Bi) with alpha particles. The origin of the name "astatine" is the Greek word *astatos*, which means "unstable."

Astatine is found in only vanishingly small amounts in nature—it is believed that only 30 grams (1 ounce) of the element are present in Earth's crust at any one time. It is produced naturally when the elements uranium and thorium decay. Astatine can also be produced in a nuclear reactor by the method used by its discoverers, according to the following reaction:

$$^{209}_{83}\mathrm{Bi} + {}^{4}_{2}\mathrm{He} \rightarrow {}^{211}_{85}\mathrm{At} + 2\,{}^{1}_{0}\mathrm{n}$$

The most stable isotope of astatine is ^{210}At, which has a half-life of 8.1 hours. Other isotopes have mass numbers ranging from 193 to 223 and half-lives ranging from 125 nanoseconds (^{213}At) to 7.2 hours (^{211}At). Astatine is known to form interhalogen compounds with bromine (AtBr), chlorine (AtCl), and iodine (AtI). Additional compounds (HAt and CH_3At) have also been detected.

Because of its scarcity and short half-life, there were no commercial uses for astatine as of 2003. Researchers are investigating astatine as a means of treating various cancers (e.g., lethal brain tumors) and diseases. Because of its similarities to iodine, which accumulates in the thyroid, it is believed that the element could be utilized to treat certain thyroid diseases. SEE ALSO HALOGENS; RADIOACTIVITY.

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Astrochemistry

In the night sky, the expanses of space between the stars of the Milky Way appear to be empty. In fact this space is occupied by a very thin gas that is mostly hydrogen and that has mere traces (less than 0.1% by number of atoms) of other elements such as oxygen, carbon, and nitrogen. The gas is also dusty; it contains grains of dust (particulate matter) that, like an interstellar fog, impede one's view of the stars. This gas is not evenly spread in space, but is clumpy. Although on average there is approximately one hydrogen atom for every cubic centimeter of interstellar space, a clump may be one thousand or more times as dense as a comparable volume of average density. Since about 1970 astronomers have been finding that these denser regions contain a great variety of molecules; about 120 different molecular species have been identified in the interstellar medium. A few of them are listed in the accompanying table. The study of these molecules in the Milky Way and in other galaxies is called astrochemistry.

How Do Astronomers Detect These Molecules?

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

Astronomers identify interstellar atoms and molecules via **spectroscopy**. For example, interstellar sodium atoms that happen to be in a line of sight going from a point on Earth's surface toward a bright star absorb light emitted by that star at a wavelength that is characteristic of sodium atoms (about 589 nanometers; 2.3×10^{-5} inches). Most interstellar molecules are detected by spectroscopic analysis that measures absorption or emission at radio wavelengths rather than those corresponding to visual light. Astronomers use large radio telescopes to detect radiation emitted by interstellar molecules. These emissions arise because the molecules are set to rotating when they collide with each other. The molecules lose energy and slow down in their rotations by emitting radiation at wavelengths that are specific for them, such that each emission is a "signature" of one type of molecule. For example, the molecule carbon monoxide, CO, may emit at various radio wavelengths, including 2.6 millimeters (0.1 inches), 1.3 millimeters (0.05 inches), 0.65 millimeters (0.03 inches), and 0.32 millimeters (0.01 inches). Interstellar gas is usually very cold (around 10 degrees above absolute zero), but even under these conditions the molecular collisions are energetic enough to keep the molecules rotating and, therefore, emitting radiation.

Sometimes these interstellar molecules may be located in warmer regions. If the gas of which they are a part is close to a star, or becomes heated

SOME MOLECULES IDENTIFIED IN THE SPACE BETWEEN THE STARS IN THE MILKY WAY

Most Abundant Molecules	Simple Hybrides	Simple Organic Molecules	Ions and Radicals	Carbon Chains
Molecular hydrogen (H_2)	Water (H_2O)	Formaldehyde (H_2CO)	CH^+	$HC_{2n+1}N$ (n=1 −5) (Cyanopolyacetylenes)
Carbon monoxide (CO)	Methane (CH_4)	Methanol (CH_3OH)	HCO^+	
	Ammonia (NH_3)	Dimethyl ether ($(CH_3)_2O$)	H_3O^+	
	Hydrogen sulfide (H_2S)	Formic acid (HCOOH)	H_3^+	
		Ethanol (C_2H_5OH)	OH	
		Benzene (C_6H_6)	CH C_nH (n=2 – 8)	

About 120 types of molecules have been identified in the space between the stars in our galaxy. Some of these molecules are listed here.

because one clump collides with another, the temperature of the molecules may rise considerably, perhaps to several thousand degrees above absolute zero. In these cases, the collisions between gas molecules are correspondingly more energetic, and molecules may be set to vibrating as well as rotating. For example, a carbon monoxide molecule, CO, vibrates to-and-fro as if the two atoms are connected by a coiled spring. A vibrating molecule also eventually slows down and loses energy (unless it is involved in further collisions) by emitting radiation that is again specific to that particular molecule. In the example of CO, that radiation has a wavelength of about 4.7 micrometers (18.5×10^{-5} inches), the detection of which necessitates the use of large telescopes that are sensitive to infrared radiation.

How Are Interstellar Molecules Formed?

The Milky Way, like all other galaxies, was formed from intergalactic gas that was essentially atomic. So where do the molecules come from? One can deduce that they are not left over from the processes that formed the Milky Way because scientists can detect molecules in regions in which they are (currently) being rapidly destroyed; therefore there must be a formation process in operation now. For example, the hydroxyl molecule, OH, can be observed in rather low density interstellar gas regions (containing about 100 H atoms per cubic centimeter) in which it is being destroyed by stellar radiation in a time frame, typically, of ten thousand years. This seems a long time but because the Galaxy has been in existence for a much longer time (about 15 billion years), the OH radicals (and many other species) must have been formed relatively recently in the Galaxy's history.

Simple collisions between O and H atoms do not lead to the formation of OH molecules, because the atoms bounce apart before they are able to form a chemical bond. Similarly, low temperature collisions between O atoms and H_2 molecules are also unreactive.

Astronomers have now determined that much of the chemistry of interstellar space occurs via ion-molecule reactions. Cosmic rays (fast-moving protons and electrons pervading all of interstellar space) ionize molecular hydrogen (H_2) and the resulting ions (H_2^+) react quickly with more H_2 to form other ions (H_3^+). The H_3^+ ions drive a chemistry that consists of simple two-body reactions. The extra proton in H_3^+ is quite weakly bound (relative to the bonding of one proton to another in H_2); in a collision an H_3^+ molecule easily donates its proton to some other species, creating a new molecule. For example, an H_3^+ ion reacts with an O atom to give OH^+, a new species:

$$O + H_3^+ \longrightarrow OH^+ + H$$

and the OH^+ then reacts with H_2 molecules to make, successively, H_2O^+ and H_3O^+ ions

$$OH^+ \longrightarrow H_2O^+ \longrightarrow H_3O^+$$

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

This process of H abstraction finishes here, because the O^+ ion in H_3O^+ has saturated all its valencies with respect to H atoms. However, the H_3O^+ ion has a strong **attraction** for electrons because of its positive charge, and the ion-electron recombination leads to dissociation of the ion-electron complex into a variety of products, including OH (hydroxyl) and H_2O (water).

Other exchange reactions occur; for example, CO may be formed through the neutral exchange

$$C + OH \longrightarrow CO + H$$

Similar ion-molecule reactions drive the chemistries of other atoms, such as C and N, to yield ions such as CH_3^+ and NH_3^+. These ions can then react with other species to form larger and more complex molecules. For example, methanol (CH_3OH) may be formed by the reaction of CH_3^+ ions with H_2O molecules, followed by recombination of the product of that reaction with electrons

$$CH_3^+ + H_2O \longrightarrow CH_3OH_2^+$$
$$CH_3OH_2^+ + e^- \longrightarrow CH_3OH + H$$

Ion-molecule reactions, followed by ion-electron recombinations and supplemented by neutral exchanges, are capable of forming the majority of the observed interstellar molecular species. Very large gas-phase reaction networks, involving some hundreds of species interacting in some thousands of chemical reactions, are routinely used to describe the formation of the observed interstellar molecules in different locations in models of interstellar chemistry.

Does the Dust Play a Role in Astrochemistry?

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

The dust has several important chemical roles. Obviously, it may shield molecules from the destructive effects of stellar radiation. It also has more active roles. We have seen that free atoms in collision may simply bounce apart before they can form a chemical bond. By contrast, atoms adsorbed on the surface of a dust grain may be held together until reaction occurs. It is believed that molecular hydrogen is formed in this way (i.e., through heterogeneous **catalysis**) and is ejected from dust grain surfaces into the gas volume with high speed and in high states of vibration and rotation. Other simple molecules, such as H_2O, CH_4, and NH_3, are also likely to form in this way.

In the denser clumps where the gas is very cold, the dust grains are also at a very low temperature (around 10 degrees above absolute zero). Gas-phase molecules colliding with such grains tend to stick to their surfaces, and over a period of time the grains in these regions accumulate mantles of ice: mostly H_2O ice, but also ices containing other molecules such as CO, CO_2, and CH_3OH. Astronomers can detect these ices with spectroscopy. For example, water ice molecules absorb radiation at a wavelength about 3.0 micrometers (11.8×10^{-5} inches), having to do with the O–H vibration in H_2O molecules; the molecules do not rotate because they are locked into the ice. In instances in which such ice-coated dust grains lie along a line of sight toward a star that shines in the infrared, this 3.0 micrometer (11.8×10^{-5} inch) absorption is very commonly seen.

Interstellar solid-state chemistry can occur within these ices. Laboratory experiments have shown that ices of simple species such as H_2O, CO, or NH_3 can be stimulated by **ultraviolet radiation** or fast particles (protons, electrons) to form complex molecules, including polycyclic aromatic hydrocarbons (PAHs) containing several benzene-type rings. The detection by astronomers of free interstellar benzene (C_6H_6) in at least one interstellar region suggests that this solid-state chemistry may be the route by which these molecules are made.

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

What Role Do Molecules Play in Astronomy?

The primary role that interstellar molecules play is a passive one: Their presence in regions so obscured by dust that we cannot see into them using optical telescopes is used to probe these regions. The most dramatic example of this is the discovery of the so-called giant molecular clouds in the Milky Way and other galaxies via the detection of the emission of 2.6 micrometers (10.2×10^{-5} inches) wavelength radiation by CO molecules present in these clouds. The existence of these huge gas clouds, containing up to a million times the mass of the Sun, was not suspected from optical observations because these clouds are completely shrouded in dust. However, radio astronomy has shown that these clouds are the largest nonstellar structures in the Galaxy, and that they will provide the raw material for the formation of millions of new stars in future billions of years of the Galaxy's evolution.

The radiation from molecules that we detect can represent a significant loss of energy from an interstellar cloud. Some molecules are very effective coolants of interstellar gases and help to maintain the temperatures of these gases at very low values. This cooling property is very important in clumps of gas that are collapsing inward under their own weight. If such a collapse can continue over vast stretches of time, then ultimately a star will form. In the early stages, it is important that the clumps remain cool, otherwise the gas pressure might halt the collapse. In these stages, therefore, the cooling effect of the molecules' emission of radiation is crucial. The formation of stars like the Sun is possible because of the cooling effect of molecules. Interstellar chemistry is therefore one factor determining the rate of star formation in the Galaxy. Astrochemists have shown that it takes about one million years for the molecules of a collapsing cloud to be formed; this is about the same amount of time as that required for the collapse itself to become established. The accompanying image illustrates a region of star formation in the Galaxy.

A star-forming region: pillars of gas in the Eagle Nebula (M16). A molecular cloud is eroded by the winds and radiation of nearby very bright stars (not shown, top right in figure), leaving these columns of denser and more resistant gas. Star formation is occurring in very dense globules of gas, some of which can be seen around the periphery of the pillars.

Astrochemistry also has a role that is particularly significant to the human species here on planet Earth. The planet was formed as a byproduct of the formation of the star that is the Sun, and is in effect the accumulation of dust grains that were the debris of large chunks of matter that subsequently impacted and stuck together. Earth is still subject to the occasional impacts of debris left over from the formation of the solar system. These impacts, now seen as a source of potential danger, in fact once brought prebiotic material to Earth. The oceans arose from the arrival of icy comets, and carbon, nitrogen, and elemental **metals** were brought by asteroid impacts. These elements and others are necessary for life on Earth, and a new discipline, astrobiology, is coming into being: Its aim is to study the transport of prebiological material in the Galaxy and the development of life within suitable environments in the universe.

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

Conclusion

Astrochemistry extends chemistry into regimes of exceptionally low density and temperature; it involves gas-phase, surface, and solid-state processes. Its products, the molecules, have opened up a new approach to astronomy. SEE ALSO SPECTROSCOPY.

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Atmospheric Chemistry

With each breath, the lungs inhale air filled with nitrogen and oxygen, the most abundant natural gases in the atmosphere. Also inhaled, however, are small quantities of gases and particles that are pollutants. Understanding the effects of these pollutants and how to control their emissions has been a continuing challenge for many centuries.

History

Humans have made a large impact on the state of the atmosphere ever since they first began using fire for light, cooking, and heat. When early populations traded their nomadic lifestyle for one based on agriculture, concentrations of air pollutants began to accumulate around permanent communities. With population growth came an increase in the use of fire, along with an increasing demand for wood.

In the twelfth and thirteenth centuries as wood became more difficult to find, growing cities began looking for alternate sources of energy. The solution was coal—plentiful, cheap, long-lasting, and hailed as the perfect new source of energy. The only "inconvenience" was the heavy black smoke that resulted from its burning. It was not long, however, before this inconvenience became a serious health concern.

As industrialization increased over the next few hundred years, the burning of coal and wood produced some of the unhealthiest air ever recorded. In some European cities, hundreds of deaths were blamed on episodes of excessive smoke and soot. London's air was especially filthy: The mixture of smoke and fog (later termed "smog") was at times so thick that it affected visibility. As little was done to control the burning of coal, many cities in Europe, Asia, and the Americas suffered from poor air quality.

Although the burning of coal remains one of the largest global sources of air pollution, the rise of automobiles in the mid-twentieth century was another major source. This was especially true on the west coast of the United States, where the ever-rising automobile population, coupled with a large petroleum industry, generated a different type of pollutant; cities became known for "brown smog," a layer of pollution that forms in sunny skies and causes irritation to the lungs and eyes.

Acid Rain

Although Earth has its own sources of naturally produced air pollutants, humans have had a far larger effect on Earth's atmosphere. One of the most striking examples of this pollution is acidic deposition, or "acid rain." Acid rain occurs when emissions of sulfur dioxide and nitrogen oxides, which typically come from coal-burning power plants and automobile emissions, react with water and oxygen to form acidic compounds such as nitric acid and sulfur-containing acids, according to the following reactions:

$$S + O_2 \rightarrow SO_2$$

$$SO_2 + O_3 \rightarrow SO_3 + O_2$$

$$SO_3 + H_2O \rightarrow H_2SO_4$$

$$SO_2 + H_2O \rightarrow H_2SO_3$$

$$2NO + O_2 \rightarrow 2NO_2$$

$$2NO_2 + H_2O \rightarrow 2HNO_3 + NO$$

$$NO + O_2 \rightarrow NO_2$$

Once airborne, these pollutants can travel long distances before returning to Earth's surface as rain or snow, or in a dry form.

Not all atmospheric acidity is due to atmospheric pollution, as Earth also has natural sources of sulfur and nitrogen. Natural sources of sulfur dioxide include volcanoes and forest fires. Air is a natural source of nitrogen oxides, as is lightning, according to the following reactions:

$$O_2 + N_2 \rightarrow 2NO$$

$$2NO + O_2 \rightarrow 2NO_2$$

Even "normal" rain (rain that has not formed in a polluted atmosphere) is acidic because of the presence of carbon dioxide in the atmosphere:

$$CO_2 + H_2O \rightarrow H_2CO_3$$

Over the millennia, normal rain has created limestone caves because calcium carbonate is slightly soluble in solutions of H_2CO_3:

$$CaCO_3\ (s) + H_2CO_3\ (aq) \rightarrow Ca(HCO_3)_2\ (aq)$$

The additional burden of human air pollution, however, has made acid rain an important environmental concern. Acid rain may acidify lakes and streams, making the water unsuitable for some fish and other wildlife. Further damage has been reported in soil and tree vegetation, which are sensitive to the acid level of rainwater.

Acid rain also speeds the decay of buildings, statues, and other man-made structures. Natural treasures such as the Taj Mahal in India, the Acropolis in Greece, and cathedrals in Germany and Britain have suffered significant damage due to acid rain. Although large sums of money are being used to help repair these structures, some damage is beyond repair.

Many governments have enacted controls on the chemicals responsible for acid rain. Although there have been some improvements in acid levels in lakes and streams, there are still many scientists who believe that stricter controls are necessary to reduce the risk to Earth's land and water.

These statues, "Saints and Sinners" by sculptor Marshall Fredericks at Oakland University, Rochester, Michigan, were exposed to acid rain. The reaction of water with sulfur dioxide and nitrogen oxides forms acidic compounds, speeding the statues' decay.

Fluorocarbons and Ozone Depletion

Ozone (O_3) is a gas consisting of three oxygen atoms. The ozone layer of the atmosphere acts as a shield protecting Earth's surface from the Sun's harmful ultraviolet (UV) radiation. When ozone absorbs UV radiation, it decomposes into an oxygen molecule (O_2) and an oxygen atom (O) as:

$$2O_3 + \text{UV radiation} \rightarrow 3O_2 + O$$

Even a relatively small decrease in the ozone layer could produce significant risks to human, animal, and plant life. For example, scientists estimated that even a 1 percent decrease in global ozone levels would produce 10,000 more cases of skin cancer each year.

Fluorocarbons are a class of chemicals widely used in various technologies, including air conditioning, aerosol cans, and fire extinguishers. While the chemicals have proved extremely useful, it was not until the 1970s (when growing concentrations of chlorine were detected in the upper atmosphere) that scientists first realized that **chlorofluorocarbons (CFCs)**, a type of fluorocarbon, could potentially destroy ozone.

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

The widespread growth of CFCs produced an unsuspecting increase in upper atmosphere chlorine. When a CFC molecule is released into the atmosphere, it can remain for many years without reacting with other chemicals. Once the CFC molecule reaches the upper atmosphere, however, it can be broken apart by UV radiation, thus releasing a chlorine atom. It is this release of chlorine that poses the serious risk to Earth's ozone layer, because it is involved in a series of ozone depleting reactions in which a chemical family or a particular species is depleted, leaving the **catalyst** unaffected. Ozone can be affected by such a cycle. In the presence of a chlorine atom (Cl), atomic oxygen and an ozone molecule are converted into molecular oxygen via the following two-step process:

catalyst: substance that aids in a reaction while retaining its own chemical identity

$$O_3 + Cl \rightarrow ClO + O_2$$

$$ClO + O \rightarrow Cl + O_2$$

A single chlorine atom can potentially destroy many thousands of ozone molecules. Notice that a chlorine atom is consumed in the first reaction and preserved in the second reaction. Chlorine atoms thus act as catalysts in the depletion of ozone.

It was not until the Antarctic ozone hole was discovered in 1985 that scientists first realized how fragile the ozone layer can be to specific chemicals. In 1987 thirty-one countries agreed to protect the ozone layer through a reduction and elimination of the chemicals that destroy ozone. This international agreement, known as the Montreal Protocol, has successfully reduced the use and production of CFCs, with the long-term goal of restoring the ozone layer to its original state.

Summary

The struggle to improve air quality has persisted for many years. Although many cities still have air pollution episodes that are classified as unhealthy, stricter emission controls mean that the air over most major cities is cleaner today than it was in the mid-twentieth century. Even so, issues such as acid rain and ozone depletion continue to pose serious environmental challenges that require cooperation between science and policy. SEE ALSO AIR POLLUTION.

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Atom Bomb *See Manhattan Project.*

Atomic Nucleus

The atomic nucleus is a tiny massive entity at the center of an atom. Occupying a volume whose radius is 1/100,000 the size of the atom, the nucleus contains most (99.9%) of the mass of the atom. In describing the nucleus, we shall describe its composition, size, density, and the forces that hold it together. After describing the structure of the nucleus, we shall go on to describe some of the limits of **nuclear** stability.

nuclear: having to do with the nucleus of an atom

The nucleus is composed of protons (charge = +1; mass =1.007 **atomic mass units** ([μ]) and neutrons. The number of protons in the nucleus is called the **atomic number** Z and defines which chemical element the nucleus represents. The number of neutrons in the nucleus is called the neutron number N, whereas the total number of neutrons and protons in the nucleus is referred to as the mass number A, where A = N + Z. The neutrons and protons are referred to collectively as nucleons. A nucleus with a given N and Z is referred to as a nuclide. Nuclides with the same atomic number are **isotopes**, such as ^{12}C and ^{14}C, whereas nuclides with the same N, such as ^{14}C and ^{16}O, are called isotones. Nuclei such as ^{14}N and ^{14}C, which have the same mass number, are isobars. Nuclides are designated by a shorthand notation in which one writes $^{A}_{Z}\textit{Chemical Symbol}_{N}$, that is, for a nucleus with 6 protons and 8 neutrons, one writes $^{14}_{6}C_{8}$, or, $^{14}_{6}C$, or just ^{14}C. The size of a nucleus is approximately 1 to 10 x 10^{-15} m, with the nuclear radius being represented more precisely as 1.2 x $A^{1/3}$ x 10^{-15} m. We can roughly approximate the nucleus as a sphere and thus we can calculate its density

atomic mass units: unit used to measure atomic mass; $\frac{1}{12}$ 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

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

$$density = \frac{mass}{volume} \cong \frac{A \bullet 1.66 \times 10^{-27}\text{kg}}{\frac{4}{3}\pi r^3} \approx \frac{A \bullet 1.66 \times 10^{-27}\text{kg}}{\frac{4}{3}\pi\left(1.2A^{1/3} \times 10^{-15}m\right)^3}$$

where 1.66 x 10^{-27} kg is the mass of the nucleon. Thus the nuclear density is about 200,000 tonnes/mm^3 and is independent of A. Imagine a cube that is 1 mm on a side. If filled with nuclear matter, it would have a mass of about 200,000 tonnes. This calculation demonstrates the enormous matter/energy density of nuclei and gives some idea as to why nuclear phenomena lead to large energy releases.

Of the 6,000 species of nuclei that can exist in the universe, about 2,700 are known, but only 270 of these are stable. The rest are radioactive, that is, they spontaneously decay. The driving force behind all **radioactive decay** is the ability to produce products of greater stability than one had initially. In other words, radioactive decay releases energy and because of the high energy density of nuclei, that energy release is substantial. Qualitatively we describe radioactive decay as occurring in three general ways: α-, β-, and γ-decay. Alpha-decay occurs in the heavy elements, and consists of the emission of a ^{4}He nucleus. Beta-decay occurs in nuclei whose N/Z ratio is different from that of a stable nucleus and consists of a transformation of neutrons into protons or vice versa to make the nucleus more stable. Gamma-decay occurs when excited nuclei get rid of some or all of their excitation energy via the emission of electromagnetic radiation, or via the radiationless transfer of energy to orbital electrons.

radioactive decay: process involving emission of subatomic particles from the nucleus, typically accompanied by emission of very short wavelength electromagnetic radiation

The force responsible for holding the neutrons and protons together within the very small nuclear volume must be unusually strong. The nuclear force, or strong interaction, is one of the four fundamental forces of nature (namely, the gravitational, electromagnetic, strong, and weak forces). The nuclear force is charge-independent, meaning that the nuclear force between two protons, or two neutrons, or a neutron and a proton, is the same. The nuclear force is short-ranged, meaning it acts over a distance of 10^{-15} to 10^{-14} m, that is, the size of nuclei. Of course the nuclear force is attractive, as it binds the nucleons in a nucleus. But some experiments have shown the nuclear force has a "repulsive core," meaning that at very short distances, the force switches from attractive to repulsive, preventing the nucleus from collapsing in on itself. The nuclear force is an "exchange" force, resulting from the virtual exchange of pions (short-lived particles with integral spin, produced normally in nuclear reactions) between interacting nucleons. More recently we have come to understand the nuclear force using a theory called quantum chromodynamics (QCD), which describes protons and neutrons as being made up of quarks. In particular, the proton is thought of as a combination of two up quarks (uu) and a down quark (d), whereas the neutron is thought to consist of one up quark (u) and two down quarks (dd). The up and down quarks are small particles with charges of $+2/3$ and $-1/3$, respectively. The quarks account for approximately 2 percent of the mass of the proton. The rest of the mass consists of gluons, which are the particles exchanged between the quarks to bind them together. The force acting between the quarks has the unusual property of being small when they are close together, and increasing as the distance between them grows. Because of this, no isolated quarks have been observed in nature.

inert: incapable of reacting with another substance

In close analogy to atomic structure, we speak of the structure of various nuclei. Many nuclear properties can be described using a nuclear shell model in which the nucleons are placed in orbitals like electrons in atoms. These orbitals and their properties are predicted by applying quantum mechanics to the problem of defining the states of the nucleons, which move under the influence of the average force in the nucleus. Like atoms, there are certain configurations of nucleons that have special stability, for example, the so-called magic numbers akin to the **inert** gas structures in chemistry. In addition to those nuclear properties that are best described in terms of a shell model, there are other properties that seem to be best explained by the large-scale collective motion of a number of nucleons. These motions lead to nuclear rotations and vibrations, which are described by a nuclear collective model.

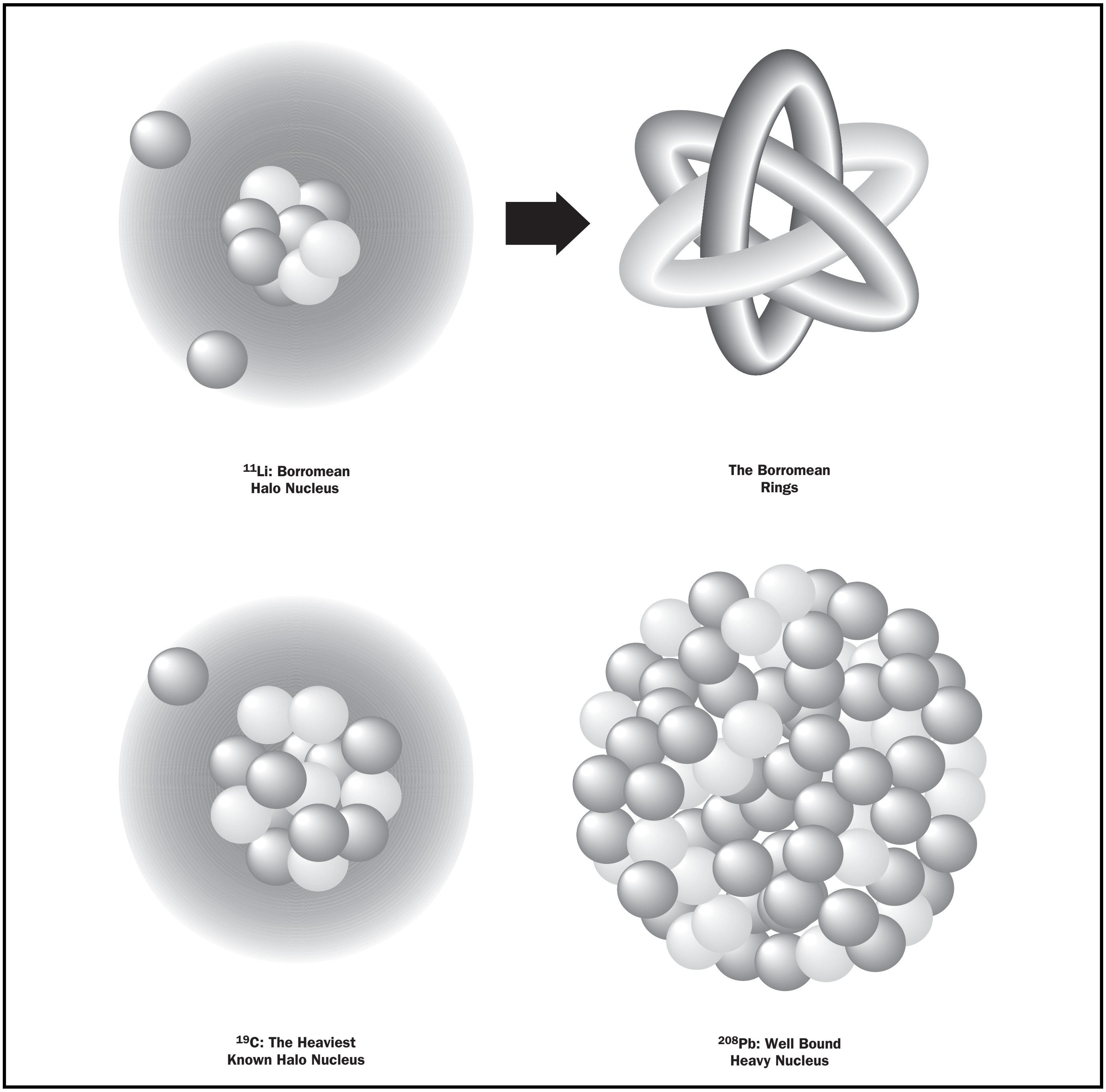
fission: process of splitting an atom into smaller pieces

synthesis: combination of starting materials to form a desired product

Current research on nuclei, their properties, and the forces that hold them together focuses on studying nuclei at the limits of stability. The basic idea is that when one studies nuclei under extreme conditions, one then has a unique ability to test theories and models that were designed to describe the "normal" properties of nuclei. One limit of nuclear stability is that of high Z, that is, as the atomic number of the nucleus increases, the repulsion between the nuclear protons becomes so large as to cause the nucleus to spontaneously **fission**. The competition between this repulsive Coulomb force and the cohesive nuclear force is what defines the size of the Periodic Table and the number of chemical elements. At present there are 112 known chemical elements, and evidence for the successful **synthesis** of elements having the atomic numbers 114 and 116 has been presented.

valence: combining capacity

Another limit of nuclear stability is the extreme of the neutron to proton ratio, N/Z. For certain very neutron-rich nuclei, such as ^{11}Li, an unusual halo structure has been observed. In halo nuclei, a "core" of nucleons is surrounded by a "misty cloud, a halo" of **valence** nucleons that are weakly bound and extend out to great distances, analogous to electrons surrounding the nucleus in an atom. Halo nuclei are fragile objects, are relatively large, and interact easily with other nuclei (have enhanced reaction cross sections). The halo nucleus ^{11}Li, which has a ^{9}Li core surrounded by a two-neutron halo is shown in Figure 1. ^{11}Li is as large as ^{208}Pb. ^{11}Li and other



^{11}Li: Borromean Halo Nucleus

The Borromean Rings

^{19}C: The Heaviest Known Halo Nucleus

^{208}Pb: Well Bound Heavy Nucleus

Figure 1. Schematic views of the nuclear halo nuclei ^{11}Li and ^{19}C that compares them to ^{208}Pb and the Borromean rings of medieval times. (Source: http://www.phy.anl.gov/ria/index)

two-neutron halo nuclei are three-body systems (2 neutrons and a ^{9}Li core), which pose a special challenge to nuclear theorists. They are also examples of Borromean systems, in which the nucleus is no longer bound if any one of the three components is removed. (The name derives from the heraldic emblem of medieval princes of Borromeo, which has three rings interlocked in such a way that removal of any one ring will make the others fall apart.) SEE ALSO Atomic Structure; Rutherford, Ernest.

Walter Loveland

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Atomic Structure

The ancient Greek philosophers Leucippus and Democritus believed that atoms existed, but they had no idea as to their nature. Centuries later, in 1803, the English chemist John Dalton, guided by the experimental fact that chemical elements cannot be decomposed chemically, was led to formulate his atomic theory. Dalton's atomic theory was based on the assumption that atoms are tiny indivisible entities, with each chemical element consisting of its own characteristic atoms.✷

✷See Atoms article for further discussion of Dalton's atomic theory.

Modern View of the Atom

The atom is now known to consist of three primary particles: protons, neutrons, and electrons, which make up the atoms of all matter. A series of experimental facts established the validity of the model. Radioactivity played an important part. Marie Curie suggested, in 1899, that when atoms disintegrate, they contradict Dalton's idea that atoms are indivisible. There must then be something smaller than the atom (subatomic particles) of which atoms were composed.

Long before that, Michael Faraday's electrolysis experiments and laws suggested that, just as an atom is the fundamental particle of an element, a fundamental particle for electricity must exist. The "particle" of electricity was given the name *electron*. Experiments with cathode-ray tubes, conducted by the British physicist Joseph John Thomson, proved the existence of the electron and obtained the charge-to-mass ratio for it. The experiments suggested that electrons are present in all kinds of matter and that they presumably exist in all atoms of all elements. Efforts were then turned to measuring the charge on the electron, and these were eventually successful by the American physicist Robert Andrews Millikan through the famous oil drop experiment.

GEORGE STONEY (1826–1911)

As a physical chemist, George Stoney made significant contributions to our understanding of molecular motion. However, this Irish scientist is better known for assigning a name to negative atomic charges, electrons, while addressing the Royal Society of Dublin in 1891.

—*Valerie Borek*

The study of the so-called canal rays by the German physicist Eugen Goldstein, observed in a special cathode-ray tube with a perforated cathode, let to the recognition in 1902 that these rays were positively charged particles (*protons*). Finally, years later in 1932 the British physicist James Chadwick discovered another particle in the nucleus that had no charge, and for this reason was named neutron.

Joseph John Thomson had supposed that an atom was a uniform sphere of positively charged matter within which electrons were circulating (the "plum-pudding" model). Then, around the year 1910, Ernest Ruthorford (who had discovered earlier that alpha rays consisted of positively charged particles having the mass of helium atoms) was led to the following model for the atom: Protons and neutrons exist in a very small nucleus, which means that the tiny nucleus contains all the positive charge and most of the mass of the atom, while negatively charged electrons surround the nucleus and occupy most of the volume of the atom.

In formulating his model, Rutherford was assisted by Hans Geiger and Ernest Marsden, who found that when alpha particles hit a thin gold foil, almost all passed straight through, but very few (only 1 in 20,000) were deflected at large angles, with some coming straight back. Rutherford remarked later that it was as if you fired a 15-inch artillery shell at a sheet of paper and it bounced back and hit you. The deflected particles suggested that the atom has a very tiny nucleus that is extremely dense and positive in charge.

Also working with Rutherford was Henry G. J. Moseley who, in 1913, performed an important experiment. When various metals were bombarded with electrons in a cathode-ray tube, they emitted X rays, the wavelengths of which were related to the nuclear charge of the metal atoms. This led to the law of chemical periodicity, which provided refinement of the periodic table introduced by Mendeleev in 1869. According to this law, all atoms of an element have the same number of protons in the nucleus. It is called the ***atomic number*** and is given the symbol Z. Hydrogen is the simplest element and has Z = 1.

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

Bohr Model of the Atom

Through Rutherford's work it was known that that electrons are arranged in the space surrounding the atomic nucleus. A planetary model of the atom, with the electrons moving in circular orbits around the nucleus seemed an acceptable model. However, such a "dynamic model" violated the laws of classical electrodynamics, according to which a charged particle, such as an electron, moving in the positive electric field of the nucleus, should lose energy by radiation and eventually spiral into the nucleus.

To solve this contradiction, in 1913, the Danish physicist Neils Bohr (then studying under Rutherford) postulated that the electron orbiting the nucleus could move only in certain orbits, having in each a certain "quantized" energy. It turns out that the colors in fireworks would help prove him right.

Atomic Spectra

The colorful lights of fireworks are emitted by "excited" atoms; that is, by atoms that have absorbed extra energy. Light consists of electromagnetic waves, each (monochromatic) color with a characteristic wavelength λ and frequency ν. Frequency is related to energy E through the famous Planck equation, $E = h\nu$, where h is Planck's constant (6.6256×10^{-34} J s). Note that white light, such as sunlight, is a mixture of light of all colors, so it does not have a characteristic wavelength. For this reason we say that white light has a "continuous spectrum." On the other hand, excited atoms emit a "line spectrum" consisting of a set of monochromatic visible radiations.

Each element has a characteristic line spectrum that can be used to identify the element. Note that line emission spectra can also be obtained by heating a salt of a metal with a flame. For instance, common salt (sodium chloride) provides a strong yellow light to the flame coming from excited sodium, while copper salts emit a blue-green light and lithium salts a red light. The colors of fireworks are due to this phenomenon.

Scientists in the late nineteenth century tried to quantify the line spectra of the elements. In 1885 the Swedish school teacher Johann Balmer discovered a series of lines in the visible spectrum of hydrogen, the wavelengths of which could be related with a simple equation:

$$\frac{1}{\lambda} = \mathrm{k}\left(\frac{1}{\mathrm{a}^2} - \frac{1}{\mathrm{b}^2}\right)$$

in which λ is wavelength, k is constant, $a = 2$, and $b = 3, 4, 5, \ldots$ This group of lines was called the Balmer series. For the red line $b = 3$, for the green line $b = 4$, and for the blue line $b = 5$. Similar series were further discovered: in the infrared region, the Paschen series (with $a = 3$ and $b = 4, 5 \ldots$ in the above equation), and much later in the ultraviolet region, the Lyman series (with $a = 1$ and $b = 2, 3 \ldots$). In 1896 the Swedish spectroscopist Johannes Rydberg developed a general equation that allowed the calculation of the wavelength of the red, green, and blue lines in the atomic spectrum of hydrogen:

$$\frac{1}{\lambda} = R\left(\frac{1}{\mathrm{n}_L^2} - \frac{1}{\mathrm{n}_H^2}\right)$$

where n_L is the number of the lower energy level to which an electron falls and n_H is the number of the higher energy level from which it falls. R is called the Rydberg constant ($1.0974 \times 10^{-7}\ \mathrm{m}^{-1}$). R was later shown to be equal to $2\pi^2 me^4\mathrm{Z}^2/h^3\mathrm{c}$, where m is the mass of the electron, e is its charge, Z is the atomic number, h is Planck's constant, and c is the speed of light.

Bohr's Quantum Model

As noted earlier, Bohr had suggested the quantization of Ruthford's model of the atom. Although he was not aware of the work of Balmer and Paschen when he wrote the first version of his 1913 article, he had incorporated Planck's constant h into his model, which turned out to be an important decision. Bohr assumed that the absorption or emission of radiation can occur only by "jumps" of the electron from one stationary orbit to another. (See Figure 1.) The energy differences between two such allowed orbits then provided the characteristic frequencies of the emitted light.

$$\Delta E = E_{\mathrm{n1}} - E_{\mathrm{n2}} = h\nu$$

Planck's constant h was named by Bohr the "quantum of action."

Bohr's theory was in close agreement with many experimental facts regarding one-electron atoms (the hydrogen atom and hydrogen-like atoms, such as He^+ and Li^{2+}), but it could not explain the "fine structure" of the spectral lines; that is, the fact that certain lines were actually a set of closely spaced lines. In 1915 and 1916 respectively, W. Wilson and A. Sommerfeld refined Bohr's theory by admitting elliptical orbits. However, it became evident to many physicists, including Bohr himself, that is was time for a scientific revolution.

Wave Character of Matter

To explain the photoelectric effect (the flow of electric current from a metal cathode when illuminated with visible or untraviolet light of suitable frequency), Albert Einstein attributed particulate (material) properties to light.

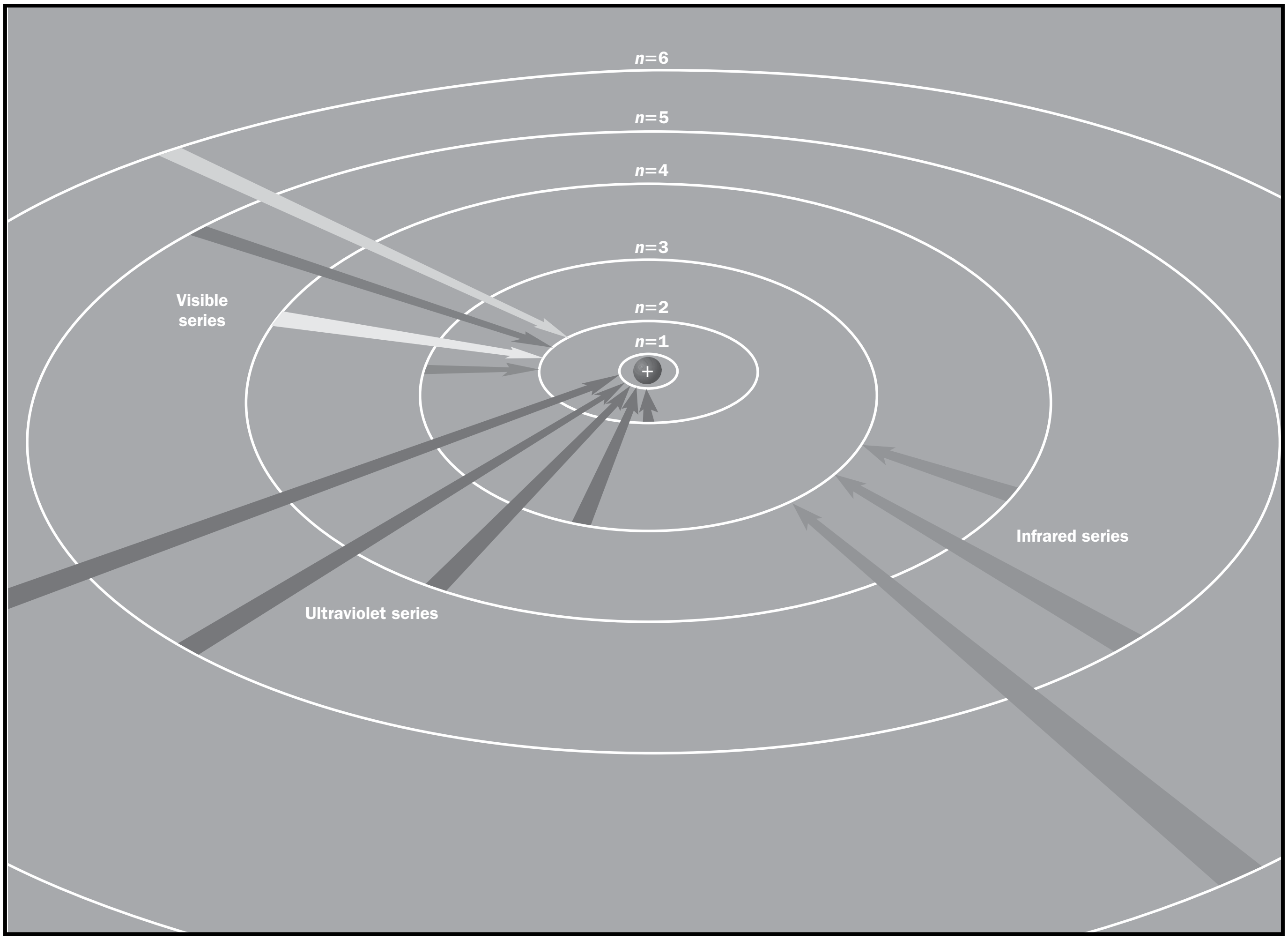


Figure 1. Diagram showing the electron jumps producing the spectral lines in the Balmer (visible) series, the Paschen (infrared) series, and the Lyman (ultraviolet) series.

Thus, besides being an electromagetic wave, light could be accounted for in terms of particles called photons. This dual property of light led the French physicist Luis Victor de Broglie to propose, in 1925, that matter should have dual character too, exhibiting both particulate and wave properties. De Broglie's genius idea was soon after (in 1927) verified by experiment.

Schrödinger's Equation: Wave Mechanics

In 1926 the Austrian physicist Erwin Schrödinger published his famous equation. He started with de Broglie's concept of matter-waves and concluded that classical mechanics is not applicable to micromechanical problems. For a single particle moving in a field that gives it a potential energy V (e.g., a one-electron atom) the Schrödinger equation takes the following form:

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} + \frac{8\pi^2 m}{h^2}(E - V) = 0$$

where ψ is generally called the wave function, m is the particle's mass, h is Planck's constant, E is the particle's total energy, and V is its classical potential energy.

CLASSICAL AND QUANTUM PHYSICS

A fundamental difference between classical and quantum physics is that, while in classical physics the dynamic variables can be represented by ordinary algebraic variables, in quantum physics they are represented by "operators," which are expressed by mathematical matrices. This is a consequence of the fact that, while in classical physics any disturbance caused by the action of observation or measurement can, in principle, be calculated, in the submicroscopic world, the very action of observation or measurement of a dynamic variable disturbs the system. This is equivalent to the famous "uncertainty principle" of Heisenberg. The distinction between quantum (very small) and classical systems is generally made in units of *h*, Planck's contant. The size of *h* 96.6256 x 10−34 js) is extremely small for the macroscopic world, but for the sumicroscopic world of atoms, ions, molecules, etc., h is not small. Thus quantum mechanics is radically different from classical mechanics.

The Schrödinger Equation in Chemistry

The Schrödinger equation is the foundation of quantum mechanics. It is solved exactly for very few simple systems. In chemistry it is solvable without any approximation only for the hydrogen atom or hydrogen-like atoms (monoelectronic atomic cations). The mathematical solutions are called hydrogen orbitals, in general, an orbital is defined as a "one-electron wave function that obeys certain mathematical restrictions." Hydrogen orbitals depend on the values of the three quantum numbers—n (principal), l (angular momentum or "asimuthal"), and m_l (magnetic).

The principal quantum number, n, identifies an electron's main shell, or energy level, and assumes integer values (1, 2, 3...). The azimuthal (or angular momentum) quantum number, l, describes the subshell, or sublevel, occupied by the electron and has values that depend on n, taking values from 0 to $n-1$. For *s* orbitals $l = 0$; for *p* orbitals $l = 1$; for *d* orbitals $l = 2$; and for the more complex *f* orbitals $l = 3$. Finally the magnetic quantum number, m_l, identifies the particular orbital an electron is in and has values that depend on l, taking on values from 0 to $+l$ or $-l$. For a given value of n, there can be only one *s* orbital, but there are three kinds of *p* orbitals, five kinds of *d* orbitals, and seven kinds of *f* orbitals.

Although it does not follow from the Schrödinger equation, there is a fourth quantum number, m_s, that describes the spin of the electron. It can assume two values, +1/2 and −1/2. According to the Pauli Exclusion Principle no two electrons in an atom can have the same set of four quantum numbers. If two electrons have the same values for n (main shell), l (subshell), and m_1 (orbital), they must differ in spin. Each orbital in an atom can hold no more than two electrons, and they must be opposed in spin. Such a couple of electrons, opposite in spin, constitutes an electron pair.

For practical reasons, various graphical representations of atomic orbitals are used. The most useful are boundary surfaces, such as those shown in Figure 2. These enclose regions of space where the electron described by the corresponding wave function (orbital) can be found with high probability (e.g., 99%); *s* orbitals are spherical, *p* orbitals are dumb-bell shaped, *d* orbitals have a four-leaf-clover shape, while *f* orbitals have complex shapes.

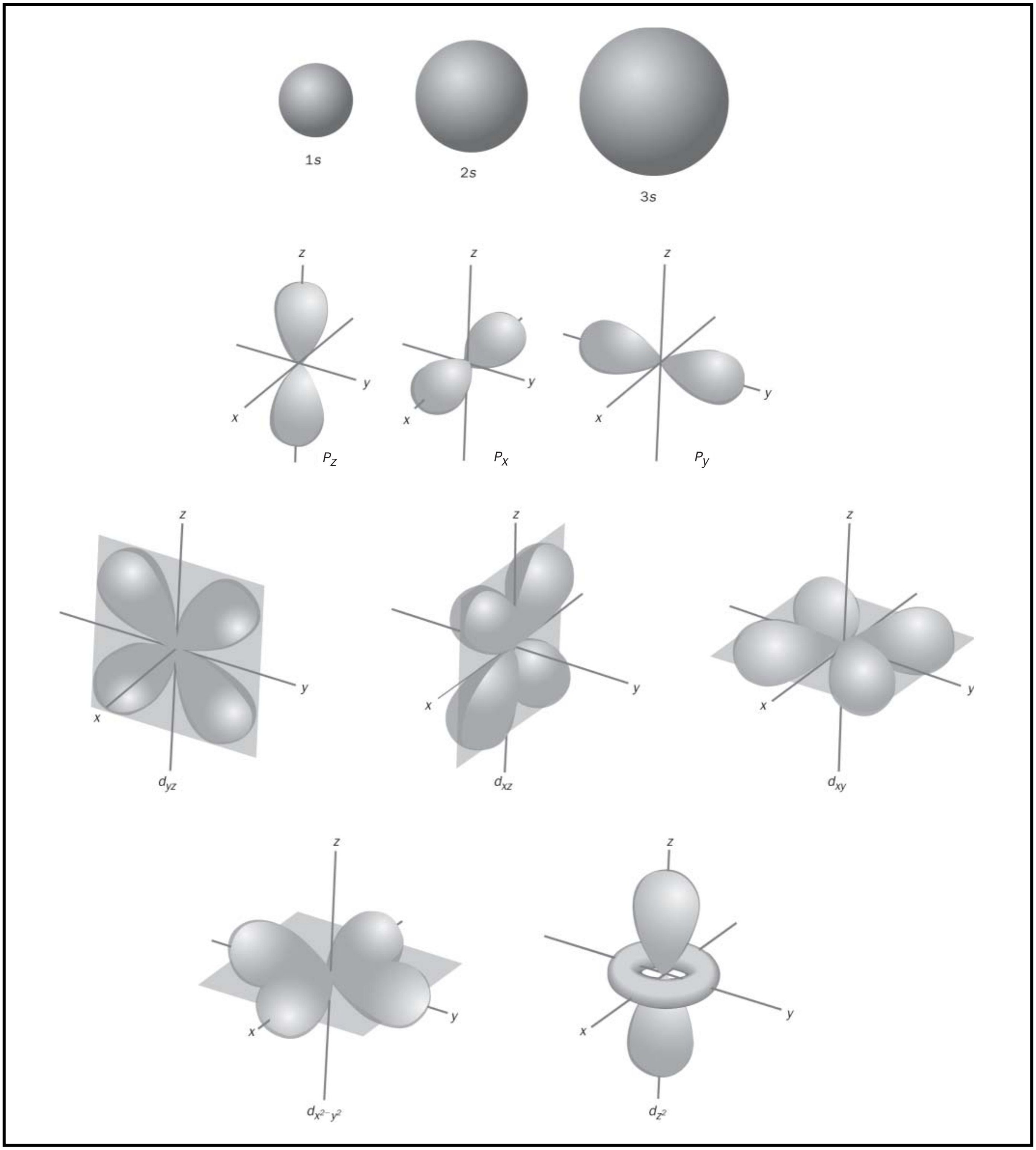


Figure 2. Orbital shapes representing boundary surfaces enclosing regions of space where electrons are most likely to be found in the first three shells.

For many-electron atoms, no exact solutions to the corresponding Schrödinger equation exist because of the electron-electron repulsions. However, various approximations can be used to locate the electrons in these atoms. The common procedure for predicting where electrons are located in larger atoms is the Aufbau (building up) principle.

The Aufbau Principle

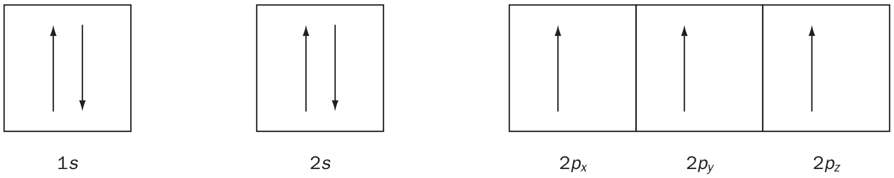
The arrangement of electrons in electron shells (K, L, M, N) is important for explaining both the chemical behavior of the elements and their placement in the periodic table. The first shell is called K ($n = 1$), the second L ($n = 2$), the third M ($n = 3$), etc. Knowing the atomic number of an element, one places that number of electrons, one after another, into the various atomic orbitals, building up the atom until all the electrons have been added.

Three basic principles are followed:

- the principle of least energy (electrons seek the lowest available energy level),
- the Pauli exclusion principle (no more than two electrons per orbital), and
- Hund's rule (electrons of the same energy spread out before pairing up).

The principle of least energy would dictate that all electrons be located in the lowest energy K shell, in the 1*s* orbital. However, the Pauli principle forbids this by requiring that no two electrons in an atom can be described by the same set of four quantum numbers. This leads to the restriction that an orbital cannot accommodate more than two electrons, and they must be of opposite spin. In this way, for a given value of *n*, the *s* orbital can accommodate no more than two electrons, the three *p* orbitals up to six electrons, the five *d* orbitals up to ten electrons, and the seven *f* orbitals up to fourteen electrons.

Hund's rule introduces one final restriction: electrons in degenerate (same energy) orbitals should spread out to fill as many orbitals as possible before pairing up. The seven electrons in the nitrogen atom would be placed in the 1*s*, 2*s*, and 2*p* sublevels as shown below. (Electrons are shown as up-pointing arrows with spin $= +\frac{1}{2}$, or down pointing arrows with spin $= -\frac{1}{2}$).



The lowest energy 1*s* orbital fills first, then the 2*s* orbital, then the last three electrons go into the three higher energy 2*p* orbitals. In a hydrogen atom all orbitals within the same main shell have the same energy, but this is not true for atoms with many electrons because of the interactions among the electrons. Within a given main shell of a large atom, the *s* orbital is the lowest in energy, followed by the *p* orbitals, then the *d* orbitals, and finally the *f* orbitals. (See Figure 3.)

electron configuration: the arrangement of electrons in an atom

The **electron configurations** of atoms are more commonly shown as follows:

$$\text{Nitrogen } (z = 7\ldots)\ 1s^2 2s^2 2p^3$$

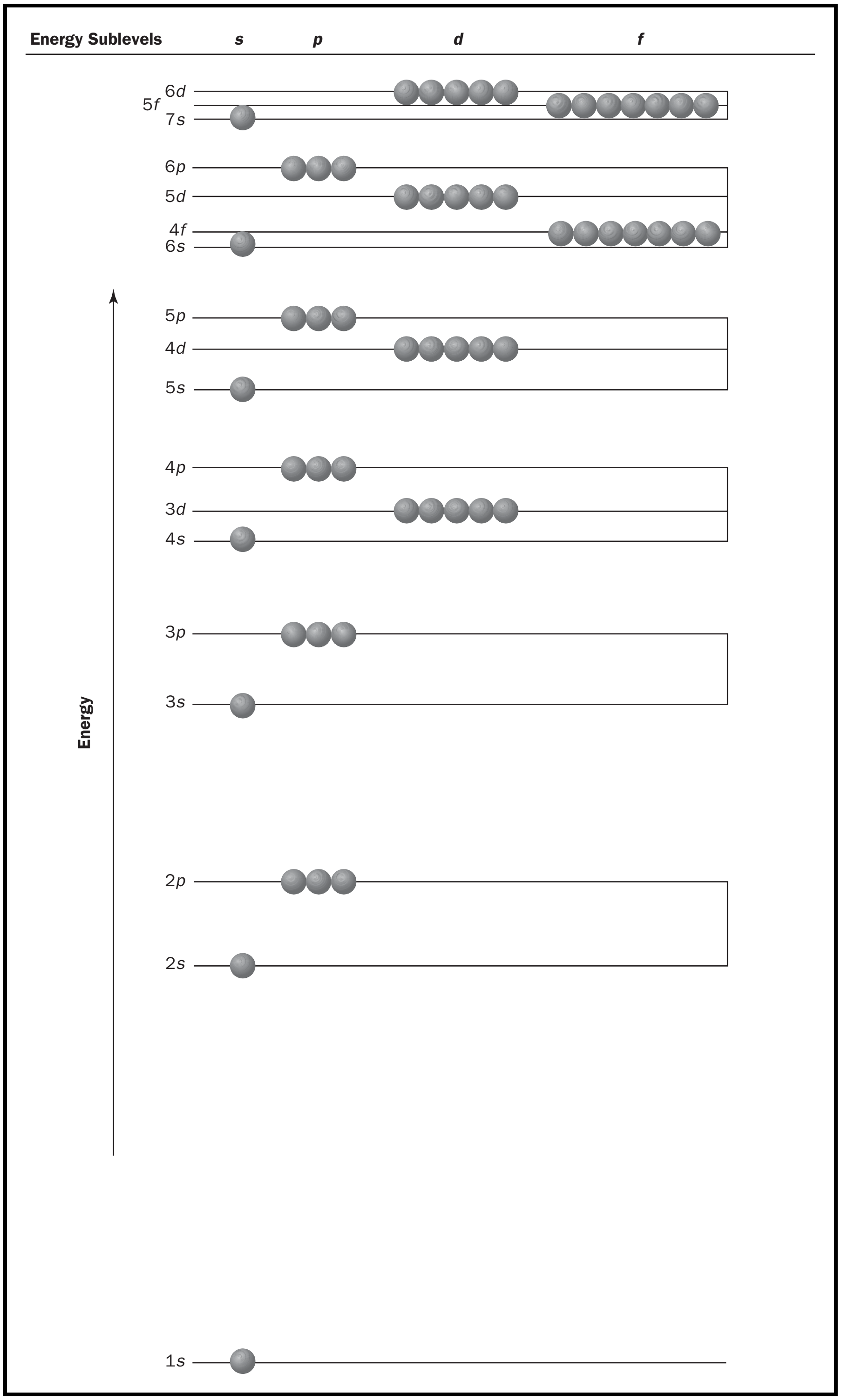


Figure 3. Relative energies of the various electron orbitals.

This shows that the nitrogen atom has a nuclear charge of +7, and it therefore has seven electrons. Two electrons are in the first main shell in an *s* orbital, and the other five are in the second main shell, two in the *s* orbital and three in the p_x, p_y, and p_z orbitals. Each can have as many kinds of orbitals (subshells) as the shell number. The first shell has one (*s*), the second has two (*s* and *p*), the third has three (*s*, *p*, and *d*), and the fourth has four (*s*, *p*, *d*, and *f*). The fifth would probably have five, if there were any atoms big enough to have a full fifth shell.

As atoms get larger, the order of filling electrons into orbitals gets more complicated. In the element Scandium (Sc), for example, the 4*s* orbital is considered filled before the 3*d* orbitals begin to fill. This may be explained in terms of the difference in shielding of the nucleus by the *s* and *d* electrons, as well as of interelectronic repulsion effects. It thus appears as if the 4*s* orbital is lower in energy than the 3*d* orbitals. (See Figure 3). The general order of filling of the various subshells is:

$1s<2s<2p<3s<3p<4s<3d<4p<5s<4d<5p<6s<4\mathrm{f}>5d<6p<7s<5f<6d<7p$

The *d* electrons always come in one shell late, and the *f* electrons two shells late. This can be demonstrated with the lead (Pb) atom. Using the Aufbau procedure to show the order of filling, the electron configuration for the Pb atom is:

Lead (Pb, Z = 82): $1s^{2}2s^{2}2p^{6}3s^{2}3p^{6}4s^{2}3d^{10}4p^{6}5s^{2}4d^{10}5p^{6}6s^{2}4f^{14}5d^{10}6p^{2}$

Perhaps the easiest way to determine the correct filling order is to use the periodic table. (See Figure 4). The square for each element represents the most recently added electron. In the first shell there are two *s* electrons; in the second there are two *s* and six *p* electrons; and in the third there are two *s* and six *p* electrons, and then ten more fill up the 3*d* orbitals after the fourth shell has begun. The transition elements result from electrons filling in the *d* orbitals, and the lanthanide and actinide elements from electrons filling in the *f* orbitals.

Electron configurations for the various elements in group 5A of the periodic table (but not indicating the order of the filling) are shown below:

Nitrogen (N, Z = 7): $\mathrm{ls^{2}2s^{2}2p^{3}}$
Phosphorus (P, Z = 15): $\mathrm{1s^{2}2s^{2}2p^{6}3s^{2}3p^{3}}$
Arsenic (As, Z = 33): $\mathrm{1s^{2}2s^{2}2p^{6}3s^{2}3p^{6}3d^{10}4s^{2}4p^{3}}$
Antimony (Sb, Z = 51): $\mathrm{1s^{2}2s^{2}2p^{6}3s^{2}3p^{6}3d^{10}4s^{2}4p^{6}4d^{10}5s^{2}5p^{3}}$
Bismuth (Bi, Z = 83): $\mathrm{ls^{2}2s^{2}2p^{6}3s^{2}3p^{6}3d^{10}4s^{2}4p^{6}4d^{10}4f^{14}5s^{2}5p^{6}5d^{10}6s^{2}6p^{3}}$

Note that the electron configurations for the larger atoms can get rather cumbersome, but they can be readily shortened by using the noble gas core convention.

Nitrogen	[He] $\mathrm{2s^{2}2p^{3}}$
Phosphorus	[Ne] $\mathrm{3s^{2}3p^{3}}$
Arsenic	[Ar] $\mathrm{3d^{10}4s^{2}4p^{3}}$
Antimony	[Kr] $\mathrm{4d^{10}5s^{2}5p^{3}}$
Bismuth	[Xe] $\mathrm{4f^{14}5d^{10}6s^{2}6p^{3}}$

The noble gas core represents all electrons contained in an atom of noble gas. The similar chemical properties of the elements in the 5A group is attibuted to the similar arrangement of the outer shell electrons of all the members of the group: $\mathrm{ns^{2}np^{3}}$. The outermost shell is vital for determining the chemical properties of the elements and is called the *valence shell*. Similar regularities appear in the other groups of the periodic table.

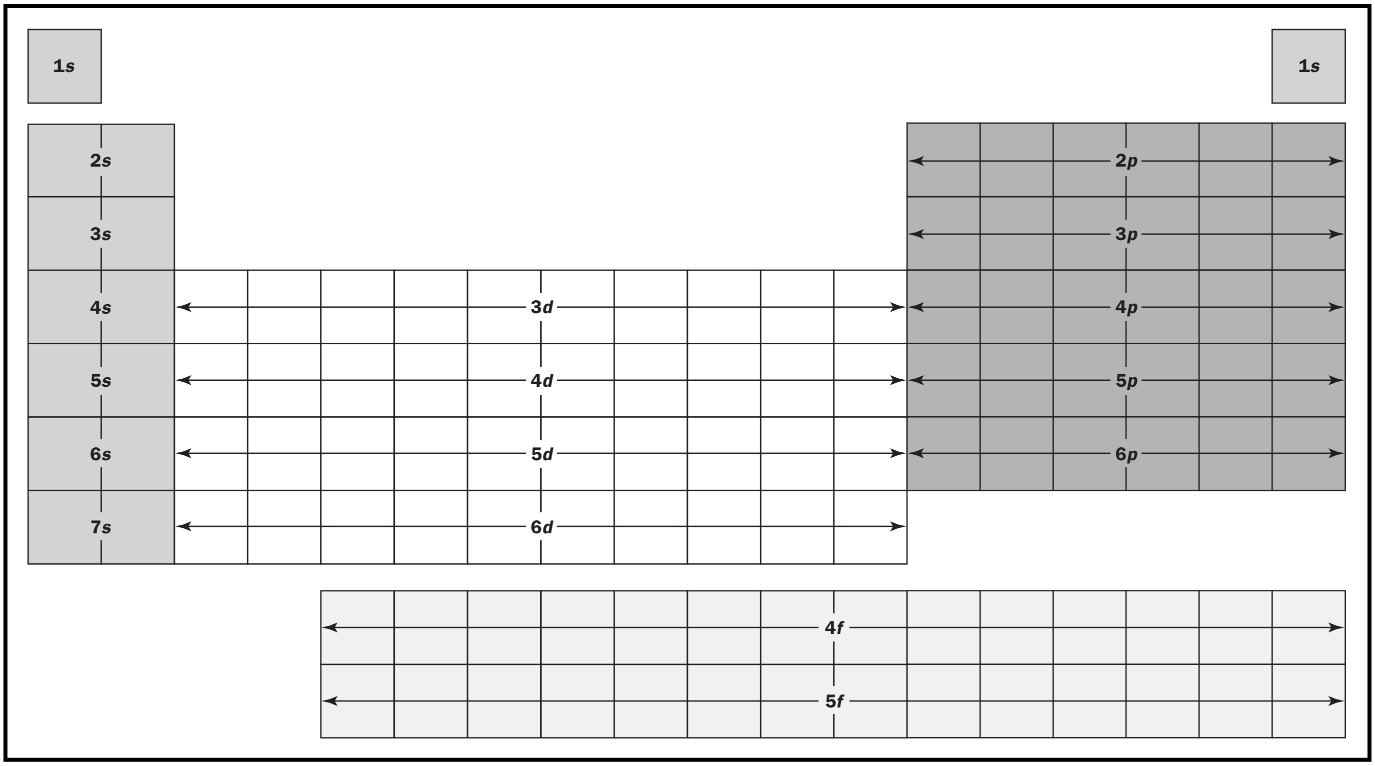


Figure 4. Diagram of the Periodic Table based on electron configurations, showing the representative elements (*s* and *p* blocks), the transition elements (*d* block), and the lanthanide and actinide elements (*f* block).

A number of elements show deviations from the predicted configurations. For instance, instead of the predicted configuration KL...$(n\text{-}1)d^4ns^2$, we have KL...$(n\text{-}1)d^5ns^1$ for the chromium (Cr) and molybdenum (Mb). In such cases, we speak of the preferred stability of the half-filled (d^5) or filled (d^{10}) *d* subshell. It might also be noted that with atoms of the heavy elements relativistic effects play a role, because of the higher velocities (approaching the speed of light) of the inner shell electrons, caused by the high Z values and the accompanying contraction of the inner shells. SEE ALSO Atomic Nucleus; Bohr, Niels.

Georgios Tsaparlis

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Atoms

An atom is the smallest possible unit of an element. Since all forms of matter consist of a combination of one or more elements, atoms are the building blocks that constitute all the matter in the universe. Currently, 110 different elements, and thus 110 different kinds of atoms, are known to exist.

Our current understanding of the nature of atoms has evolved from the ancient, untested ideas of Greek philosophers, partly as a result of modern technology that has produced images of atoms.

The Greek Atomistic Philosophy

The earliest ideas concerning atoms can be traced to the Greek philosophers, who pursued wisdom, knowledge, and truth through argument and reason. Greek scientific theories were largely based on speculation, sometimes based on observations of natural phenomena and sometimes not. The idea of designing and performing experiments rarely occurred to Greek philosophers, to whom abstract intellectual activity was the only worthy pastime.

atomic theory: physical concept that asserts that matter is composed of microscopically tiny particles called atoms and that various elements differ from each other by having different atoms

Empedocles, a Greek philosopher active around 450 B.C., proposed that there were four fundamental substances—earth, air, fire, and water—which, in various proportions, constituted all matter. Empedocles, thus, formulated the idea of an elemental substance, a substance that is the ultimate constituent of matter; the chemical elements are modern science's fundamental substances. An **atomic theory** of matter was proposed by Leucippus, another Greek philosopher, around 478 B.C. Our knowledge of the atomic theory of Leucippus is derived almost entirely from the writings of his student, Democritus, who lived around 420 B.C. Democritus maintained that all materials in the world were composed of *atoms* (from the Greek *atomos*, meaning indivisible). According to Democritus, atoms of different shapes, arranged and positioned differently relative to each other, accounted for the different materials of the world. Atoms were supposed to be in random perpetual motion in a *void;* that is, in nothingness. According to Democritus, the feel and taste of a substance was thought to be the effect of the atoms of the substance on the atoms of our sense organs. The atomic theory of Democritus provided the basis for an explanation of the changes that occur when matter is chemically transformed. Unfortunately, the theory was rejected by Aristotle (384–322 B.C.) who became the most powerful and famous of the Greek scientific philosophers. However, Aristotle adopted and developed Empedocles's ideas of elemental substances. Aristotle's elemental ideas are summarized in a diagram (shown in Figure 1), which associated the four elemental substances with four *qualities:* hot, moist, cold, and dry. Earth was dry and cold; water was cold and moist; air was moist and hot; and fire was hot and dry. Every substance was composed of combinations of the four elements, and changes (which we now call *chemical*) were explained by an alteration in the proportions of the four elements. One element could be converted into the other by the addition or removal of the appropriate qualities. There were, essentially, no attempts to produce evidence to support this four-element theory, and, since Aristotle's scientific philosophy held sway for 2,000 years, there was no progress in the development of the atomic concept. The tenuous relationship between elements and atoms had been severed when Aristotle rejected the ideas of Democritus. Had the Greek philosophers been open to the idea of experimentation, atomic theory, indeed all of science, could have progressed more rapidly.

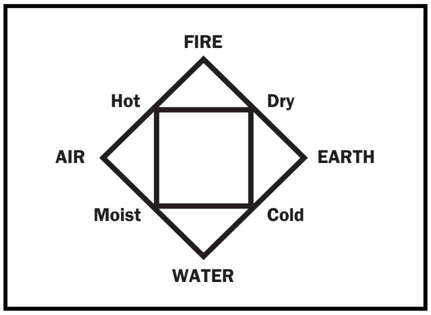


Figure 1. Aristotle's four-element diagram.

The Rise of Experimentation

The basis of modern science began to emerge in the seventeenth century, which is often recognized as the beginning of the Scientific Revolution. Conceptually, the Scientific Revolution can be thought of as a battle between three different ways of looking at the natural world: the Aristotelian, the magical, and the mechanical. The seventeenth century saw the rise of experimental science. The idea of making observations was not new. However, Sir Francis Bacon (1561–1626) emphasized that experiments should be planned and the results carefully recorded so they could be repeated and verified, an attitude that infuses the core idea of modern science. Among the early experimentalists was Robert Boyle (1627–1691), who studied quantitatively the compression and expansion of air, which led him to the idea that air was composed of particles that he called *corpuscles*, which he maintained were in constant motion. Boyle's description of corpuscular motion presages the kinetic molecular theory.

The Chemical Atom

An atomic theory based on chemical concepts began to emerge from the work of Antoine Lavoisier (1743–1794), whose careful quantitative experiments led to an operational definition of an element: An element was a substance that could not be decomposed by chemical processes. In other words, if a chemist could not decompose a substance, it must be an element. This point of view obviously put a premium on the ability of chemists to manipulate substances. Inspection of Lavoisier's list of elements, published in 1789, shows a number of substances, such as silica (SiO_2), alumina (Al_2O_3), and baryta (BaO), which today are recognized as very stable compounds. The chemists of Lavoisier's time simply did not have the tools to decompose these substances further to silicon, aluminum, and barium, respectively. The composition of all compounds could be expressed in terms of the elemental substances, but it was the quantitative mass relationship of compounds that was the key to deducing the reality of the chemical atom.

DEMOCRITUS OF ABBERA

Little is known for certain about Democritus of Abbera (c.460 B.C.E.–c.362 B.C.E. None of his writings has survived intact. It is known from others (both students and detractors) that Democritus was one of the earliest advocates of a theory that all matter exists as collections of very small, permanent, indivisible particle called atoms.

—David A. Bassett

Lavoisier's successful use of precise mass measurements essentially launched the field of analytical chemistry, which was thoroughly developed by Martin Klaproth (1743–1817). Lavoisier established the concept of mass conservation in chemical reactions, and, late in the eighteenth century, there was a general acceptance of the concept of definite proportions (constant composition) in chemical compounds, but not without controversy. Claude-Louis Berthollet (1748–1822) maintained that the composition of compounds could be variable, citing, for example, analytical results on the oxides of copper, which gave a variety of results, depending on the method of **synthesis**. Joseph-Louis Proust (1754–1826), over a period of eight years, showed that the variable compositions, even with very accurate analytical data, were due to the formation of different mixtures of two oxides of copper, CuO and Cu_2O. Each oxide obeyed the law of constant composition, but reactions that were supposed to lead to "copper oxide" often produced mixtures, the proportions of which depended on the conditions of the reaction. Proust's proof of the law of constant composition was important, because compounds with variable composition could not be accommodated within the evolving chemical atomic theory.

synthesis: combination of starting materials to form a desired product

John Dalton (1766–1844), a self-educated English scientist, was primarily interested in meteorology and is credited with being the first to describe color blindness, a condition with which he was burdened throughout his life. Color blindness is a disadvantage for a chemist, who must be able to see color changes when working with chemicals. Some have suggested that his affliction was one reason why Dalton was a rather clumsy and slipshod experimenter. Gaseous behavior had been well established, starting with the experiments of Boyle. Dalton could not help supposing, as others previously did, that gaseous matter was composed of particles. But Dalton took the next and, ultimately, most important steps in assuming that *all* matter—gaseous, liquid, and solid—consists of these small particles. The law of definite proportions (constant composition) as articulated by Proust, suggested to Dalton that a compound might contain two elements in the ratio of, for example, 4 to 1, but never 4.1 to 1 or 3.9 to 1. This observation could easily be explained by supposing that each element was made up of individual particles.

Dalton's atomic theory can be succinctly summarized by the following statements:

> Elements are composed of extremely small particles called *atoms.*
>
> All atoms of a given element have identical properties, and those properties differ from those of other elements.
>
> Compounds are formed when atoms of different elements combine with one another in small whole numbers.
>
> The relative numbers and kinds of atoms are constant in a given compound.

Dalton recognized the similarity of his theory to that of Democritus, advanced twenty-one centuries earlier when the Greek philosopher called these small particles *atoms*, and, presumably, implied by using that word that these particles were indivisible. In Dalton's representation (Figure 2) the elements were shown as small spheres, each with a separate identity. Compounds of elements were shown by combining the appropriate elemental representations in the correct proportions, to produce complex symbols that seem to echo our present use of standard chemical formulas. Dalton's symbols—circles with increasingly complex inserts and decorations—were not adopted by the chemical community. Current chemical symbols (formulas) are derived from the suggestions of Jöns Berzelius (1779–1848). Berzelius also chose oxygen to be the standard reference for atomic mass (O = 16.00 AMU). Berzelius produced a list of atomic masses that were much closer to those that are currently accepted because he had developed a better way to obtain the formulas of substances. Whereas Dalton assumed that water had the formula HO, Berzelius showed it to be H_2O. The property of atoms of interest to Dalton were their relative masses, and Dalton produced a table of atomic masses (Table 1) that was seriously deficient because he did not appreciate that atoms did not have to be in a one-to-one ratio; using more modern ideas, Dalton assumed, incorrectly, that all atoms had a **valence** of one (1). Thus, if the atomic mass of hydrogen is arbitrarily assigned to be 1, the atomic mass of oxygen is 8 on the Dalton scale. Dalton, of course, was wrong, because a water molecule contains two atoms of hydrogen for every oxygen atom, so that the individual oxygen atom is eight times as heavy as two hydrogen atoms or sixteen times as heavy as a single hydrogen atom. There was no way that Dalton could have known, from the data available, that the formula for water is H_2O.

valence: combining capacity

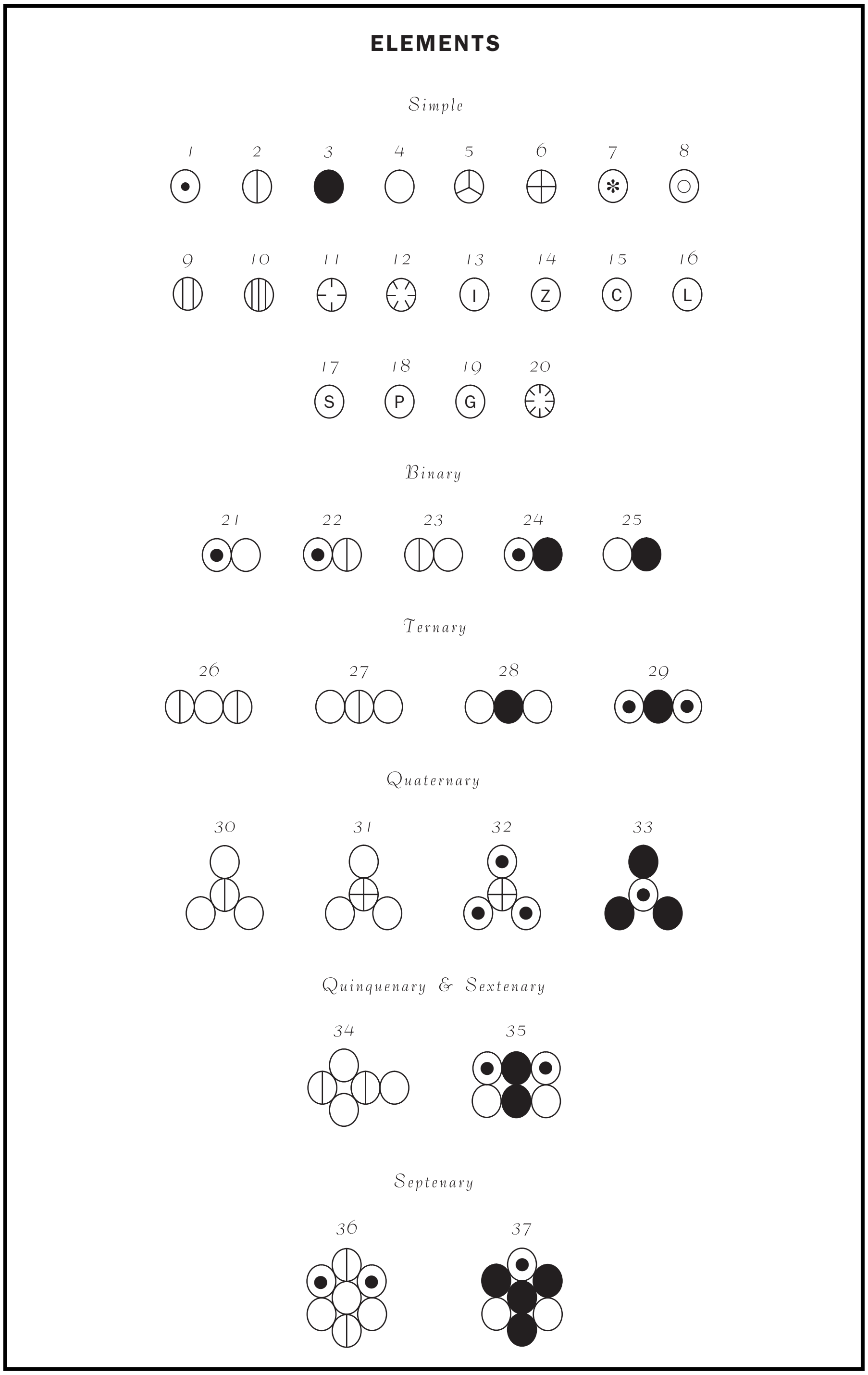


Figure 2. Dalton's atomic symbols are described as "simple." The increasingly complex combination of symbols represent binary, ternary, quaternary, etc., compounds. Thus, Number 28 is a compound atom of carbonic acid (carbon dioxide), and number 31 is a compound atom of sulphuric acid (sulphyr trioxide).

Dalton's atomic theory explained the law of multiple proportions. For example, it is known that mercury forms two oxides: a black substance containing 3.8 percent oxygen and 96.2 percent mercury, and a red compound containing 7.4 percent oxygen and 92.6 percent mercury. Dalton's theory states that the atoms of mercury (Hg) and oxygen (O) must combine in whole numbers, so the two compounds might be HgO and Hg_2O, for example. Furthermore, Dalton's theory states that each element has a characteristic mass—perhaps 9 mass units for Hg and 4 mass units for O (the

Table 1. Dalton's first set of atomic weight values (1805).

DALTON'S FIRST SET OF ATOMIC WEIGHT VALUES (1805)

Hydrogen	1
Azot	4.2
Carbon	4.3
Ammonia	5.2
Oxygen	5.5
Water	6.5
Phosphorus	7.2
Phosphuretted hydrogen	8.2
Nitrous gas	9.3
Ether	9.6
Gaseous oxide of carbon	9.8
Nitrous oxide	13.7
Sulphur	14.4
Nitric acid	15.2
Sulphuretted hydrogen	15.4
Carbonic acid	15.3
Alcohol	15.1
Sulphureous acid	19.9
Sulphuric acid	25.4
Carburetted hydrogen from stagnant water	6.3
Olefiant gas	5.3

numbers were chosen arbitrarily, here). Given these assumptions, the relevant concepts are shown in Table 2.

The *assumed* formulas are presented in line 1. The percent composition of each compound, calculated in the usual way, is presented in line 3, showing that these two compounds, indeed, have different compositions, as required by the law of multiple proportions. Line 4 contains the ratio of the mass of mercury to the mass of oxygen, for each compound. Those ratios can be expressed as the ratio of simple whole numbers (2.25:4.5 = 1:2), fulfilling a condition required by the law of multiple proportions. Notice that Dalton's ideas do not depend upon the values assigned to the elements or the formulas for the compounds involved. Indeed, the question as to which compound, red or black, is associated with which formula cannot be answered from the data available. Thus, although Dalton was unable to establish an atomic mass scale, his general theory did provide an understanding of the three mass-related laws: conservation, constant composition, and multiple proportion. Other information was required to establish the relative masses of atoms.

The other piece of the puzzle of relative atomic masses was provided by Joseph-Louis Gay-Lussac (1778–1850), who published a paper on volume relationships in reactions of gases. Gay-Lussac made no attempt to interpret his results, and Dalton questioned the paper's validity, not realizing that the law of combining volumes was really a verification of his atomic theory! Gay-Lussac's experiments revealed, for example, that 2 volumes of carbon monoxide combine with 1 volume of oxygen to form 2 volumes of carbon dioxide. Reactions of other gaseous substances showed similar volume relationships. Gay-Lussac's law of combining volumes suggested, clearly, that equal volumes of different gases under similar conditions of temperature and pressure contain the same number of reactive particles (molecules). Thus, if 1 volume of ammonia gas (NH_3) combines exactly with 1 volume of hydrogen chloride gas (HCl) to form a salt (NH_4Cl), it is natural to conclude that each volume of gas must contain the same number of particles.

LAW OF MULTIPLE PROPORTIONS

Assumed formula	HgO	Hg_2O
Total mass of compound	9 + 4 = 13	9 + 9 + 4 = 22
% composition	% Hg 69.2; % O = 30.8	% Hg = 81.8; % O = 18.2
Mass Hg/Mass O	9/4 = 2.25	18/4 = 4.5

Table 2. Law of multiple proportions.

At least one of the implications of Gay-Lussac's law was troubling to the chemistry community. For example, in the formation of water, 2 volumes of hydrogen gas combined with 1 volume of oxygen gas to produce 2 volumes of steam (water in the gaseous state). These observations produced, at the time, an apparent puzzle. If each volume of gas contains *n* particles (molecules), 2 volumes of steam must contain 2 *n* particles. Now, if each water particle contains at least 1 oxygen atom, how is it possible to get two oxygen atoms (corresponding to 2 *n* water molecules) from *n* oxygen particles? The obvious answer to this question is that each oxygen particle contains two oxygen atoms. This is equivalent to stating that the oxygen *molecule* consists of two oxygen *atoms*, or that oxygen gas is diatomic (O_2). Amedeo Avogadro (1776–1856) an Italian physicist, resolved the problem by adopting the hypothesis that equal volumes of gases under the same conditions contain equal numbers of particles (molecules). His terminology for what we now call an atom of, for instance, oxygen, was *half molecule*. Similar reasoning involving the combining of volumes of hydrogen and oxygen to form steam leads to the conclusion that hydrogen gas is also diatomic (H_2). Despite the soundness of Avogadro's reasoning, his hypothesis was generally rejected or ignored. Dalton never appreciated its significance because he refused to accept the experimental validity of Gay-Lussac's law.

Avogadro's hypothesis—equal volumes of gases contain equal numbers of particles—lay dormant for nearly a half-century, until 1860 when a general meeting of chemists assembled in Karlsruhe, Germany, to address conceptual problems associated with determining the atomic masses of the elements. Two years earlier, Stanislao Cannizzaro (1826–1910) had published a paper in which, using Avogadro's hypothesis and vapor density data, he was able to establish a scale of relative atomic masses of the elements. The paper, when it was published, was generally ignored, but its contents became the focal point of the Karlsruhe Conference.

Cannizzaro's argument can be easily demonstrated using the compounds hydrogen chloride, water, ammonia, and methane, and the element hydrogen, which had been shown to be diatomic (H_2) by using Gay-Lussac's reasoning and his law of combining volumes. The experimental values for vapor density of these substances, all determined under the same conditions of temperature and pressure, are also required for Cannizzaro's method for establishing atomic masses. The relevant information is gathered in Table 3. The densities of these gaseous substances (at 100° C and one atmosphere pressure) are expressed in grams per liter. The masses of the substances (in one liter) are the masses of equal numbers of molecules of each substance; the specific number of molecules is unknown, of course, but that number is unnecessary for the Cannizzaro analysis. If that unknown number of molecules is called N, and if m_H represents the mass of a single hydrogen atom, then $m_H \times 2N$ is the total

CANNIZZARO'S METHOD OF MOLECULAR MASS DETERMINATION

Gaseous Substance	Density g/L[1]	Relative to Mass of an H Atom (Molecular Mass, Relative to H = 1)	% Hydrogen	Relative Mass of H Present	Number H Atoms Present in a Molecule	Formula	Mass of "Other" Atoms
Hydrogen	0.0659	2.00	100	2.00	2	H_2	H = 1
Hydrogen chloride	1.19	36.12	2.76	1.00	1	HCl	Cl = 35.2
Water	0.589	17.88	11.2	2.00	2	H_2O	O = 15,88
Ammonia	0.557	16.90	17.7	3.00	3	NH_3	N = 13.90
Methane	0.524	15.90	25.1	4.00	4	CH_4	C = 11.90

[1] Density reported for conditions of 100° C and one atmosphere pressure

Table 3. Cannizzaro's method of molecular mass determination.

mass of the hydrogen atoms in the 1 liter sample of hydrogen molecules; recall that hydrogen was shown to be diatomic (H_2) by Gay-Lussac's law. From this point of view, the relative masses of the molecules fall in the order of the masses in 1 liter (or their densities). The mass of the hydrogen *atom* was taken as the reference (H = 1) for the relative atomic masses of the elements. Thus, the mass of all the hydrogen chloride molecules in the one liter sample is $m_{\mathrm{HCl}}N$, and the ratio of the mass of a hydrogen chloride molecule to a hydrogen atom is given by:

$$\frac{m_{\mathrm{Cl}} \times \cancel{\mathrm{N}}}{m_{\mathrm{H}} \times 2\cancel{\mathrm{N}}} = \frac{1.19}{0.0659} = \frac{36.12}{1.00}$$

That is, if the mass of a hydrogen atom is taken to be 1 unit of mass, the mass of the hydrogen chloride molecule is 36.12 units. All the molecular masses listed in column 3 of the table can be established in the same way—twice the ratio of the density of the molecule in question to the density of hydrogen. Using experimental analytical data (column 4), Cannizzaro was able to establish the relative mass of hydrogen in each molecule (column 5), which gave the number of hydrogen atoms present in each molecule of interest (column 6), which, in turn, produced the formula of the molecule (column 7); analytical data also quantitatively indicate the *identity* of the other atom in the molecule. Thus, analysis would tell us that, for example, methane contains hydrogen and carbon. Knowing the total mass of the molecule (column 3) and the mass of all the hydrogen atoms present, the mass of the "other atom" in the molecule can be established as the difference between these numbers (column 8). Thus, if the mass of the HCl molecule is 36.12 and one atom of hydrogen of mass 1.00 is present, the mass of a Cl atom is 35.12. Relative mass units are called **atomic mass units**, AMUs.

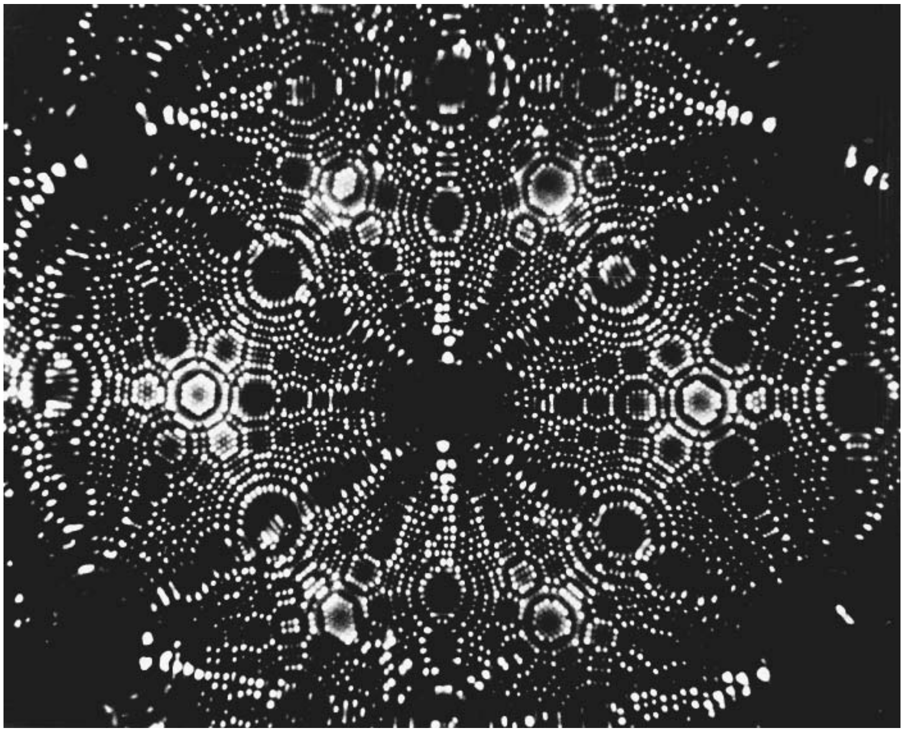
atomic mass units: unit used to measure atomic mass; $\frac{1}{12}$ of mass of a carbon-12 atom

This very convincing use of Gay-Lussac's law and Avogadro's hypothesis by Cannizzaro quickly provided the chemical community with a direct way of establishing not only the molecular formulas of binary compounds but also the relative atomic masses of elements, starting with quantitative analytical data and the density of the appropriate gaseous substances.

The long struggle to establish the concept of the chemical atom involved many scientists working in different countries using different kinds of equipment to obtain self-consistent data. All were infused with ideas of Sir Francis Bacon, who defined the classic paradigm of experimental science—results that are derived from careful observations and that are openly reported for verification. However, not all chemists equally embraced these ideas, which were to become fundamental to their craft. For example, the great physical chemist and Nobel Prize winner Friedrich Wilhelm Ostwald (1853–1932) refused to accept the existence of atoms well into the twentieth century. Ostwald held a strong personal belief that chemists ought to confine their studies to measurable phenomena such as energy changes. The atomic theory was to Ostwald nothing more than a convenient fiction.

There are, of course, other lines of observations and arguments that lead to the conclusion that matter is particulate and, subsequently, to an ultimate atomic description of matter. One of these involves the **Brownian motion** of very small particles. Robert Brown (1773–1858), a Scottish botanist, observed in 1827 that individual grains of plant pollen suspended in water moved erratically. This irregular movement of individual particles of a suspension as observed with a microscope is called *Brownian motion.* Initially, Brown believed that this motion was caused by the "hidden life" within the pollen grains, but further studies showed that even nonliving suspensions behave in the same way. In 1905 Albert Einstein (1879–1955) worked out a mathematical analysis of Brownian motion. Einstein showed that if the water in which the particles were suspended was composed of molecules in random motion according to the requirements of the kinetic molecular theory, then the suspended particles would exhibit a random "jiggling motion" arising from the occasional uneven transfer of momentum as a result of water molecules striking the pollen grains. One might expect that the forces of the water molecules striking the pollen grains from all directions would average out to a zero net force. But Einstein showed that, occasionally, more water molecules would strike one side of a pollen grain than the other side, resulting in a movement of the pollen grain. The interesting point in Einstein's analysis is that even if each collision between a water molecule and a pollen grain transfers a minuscule amount of momentum, the enormous

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



Photomicrograph of atoms in a tungsten crystal, magnified 2,700,000 times.

number of molecules striking the pollen grain is sufficient to overcome the large momentum advantage of the pollen grain (because of its considerably larger mass than that of a water molecule). Although the Swedish chemist Theodor Svedberg (1884–1971) suggested the general molecular explanation earlier, it was Einstein who worked out the mathematical details. Einstein's analysis of Brownian motion was partially dependent on the size of the water molecules. Three years later, Jean-Baptiste Perrin (1870–1942) set about to determine the size of the water molecules from precise experimental observations of Brownian motion. In other words, Perrin assumed Einstein's equations were correct, and he made measurements of the particles' motions, which Brown had described only qualitatively. The data Perrin collected allowed him to calculate the size of water molecules. Ostwald finally yielded in his objection to the existence of atoms because Perrin had a direct measure of the effect of water molecules on macroscopic objects (pollen grains). Since water was composed of the elements hydrogen and oxygen, the reality of atoms had been experimentally proved in Ostwald's view of how chemistry should be pursued.

Ostwald's reluctance to accept the chemical atom as an entity would surely have yielded to the overwhelming evidence provided by scanning tunneling microscopy (STM). Although Ostwald did not live to see it, this technique provides such clear evidence of the reality of simple atoms that even he would have been convinced. SEE ALSO Avogadro, Amedeo; Berthollet, Claude-Louis; Berzelius, Jöns JaKob; Boyle, Robert; Cannizzaro, Stanislao; Dalton, John; Einstein, Albert; Gay-Lussac, Joseph-Louis; Lavoisier, Antoine; Ostwald, Friedrich Wilhelm; Svedberg, Theodor; MOLECULES.

J. J. Lagowski

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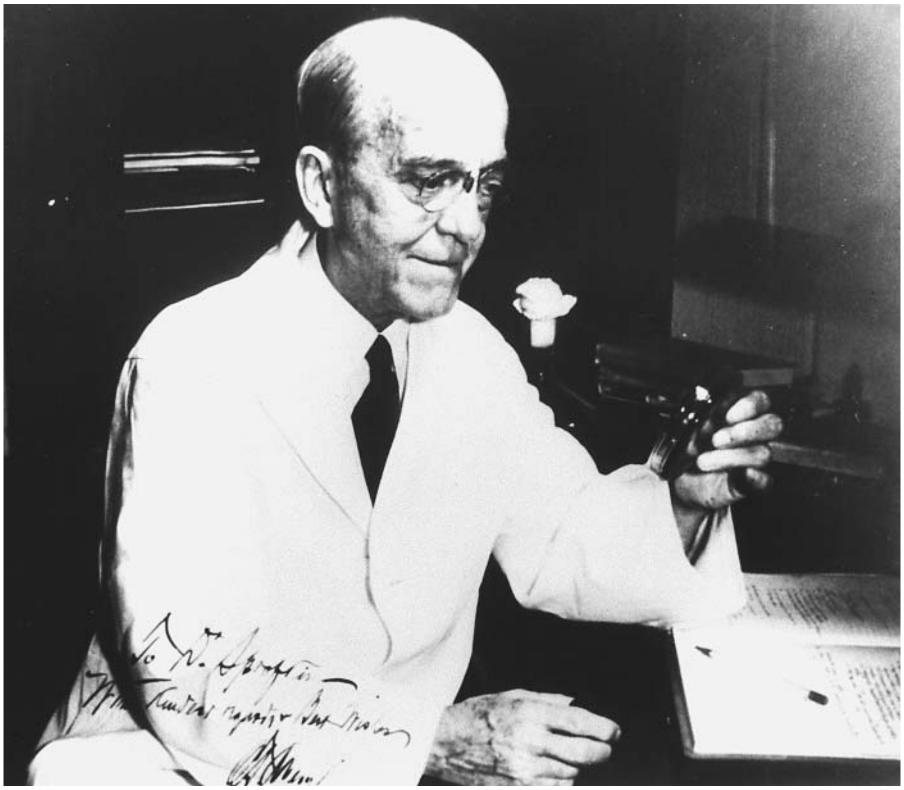
Avery, Oswald

CANADIAN-AMERICAN PHYSICIAN
1877–1955

By the early 1940s, scientists knew that chromosomes existed and that they were composed of smaller units called genes. Chemical analysis had revealed that the eucaryotic chromosome consists of about 50 percent protein and 50 percent deoxyribonucleic acid (DNA). There was no particular interest in DNA for several previous decades because no role had been assigned to it. This changed when a Canadian-born American named Oswald Avery showed that DNA is responsible for the transmission of heritable characteristics.

Avery moved from Canada to New York City in 1887. He attended Colgate University and in 1904 received his medical degree from the College of Physicians and Surgeons at Columbia University. He practiced medicine



American bacteriologist Oswald Avery, who demonstrated that DNA is the unit of genetic inheritance.

for several months before he became more interested in the transmission of infectious diseases. In 1913, Avery arrived at Rockefeller Institute, where he worked as a bacteriologist for over 43 years.

Avery and his co-workers studied the life cycle and chemical make-up of *Diplococcus pneumoniae*, or pneumococci, a species of bacteria that causes pneumonia. Avery's interest was sparked by British microbiologist Frederick Griffith's work with pneumococci. In 1928, Griffith described an experiment in which he injected mice with a mixture of a harmless strain of living pneumococci and the dead remains of a virulent strain of the bacteria. The mice died from infection by the *live* organisms of the virulent strain, though the organisms had been dead when they were administered. By 1932 Avery focused on transformation—a process by which heritable characteristics of one species are incorporated into another different species.

In an attempt to duplicate Griffith's work, Avery and his colleagues began to grow large quantities of virulent type III capsulated pneumococcus. They purified the live virulent encapsulated bacteria and then killed them by extreme heat. The bacteria's polysaccharide protein, which makes up the capsule or outer envelope, was then removed. The remaining portion of the dead bacteria, its polysaccharide gone but capsules intact, was added to living, unencapsulated bacteria. It was found that the offspring of these living bacteria had capsules. Avery had determined that the active transforming principle, as Griffith had described earlier, still remained. Because the polysaccharide protein had been removed for the test, it could not be the transforming factor.

Avery wanted to be certain that the active agent was the DNA and not a small amount of protein contamination. To verify the result, a quantity of DNase, an enzyme that would destroy the DNA without affecting the protein, was prepared and added to the sample. When a portion of bacteria was tested, it could no longer transform the unencapsulated bacteria into encapsulated bacteria. Avery and his co-workers had conclusively proven that DNA was the transforming principle responsible for the development of polysaccharide capsules in the unencapsulated bacteria.

This experiment, first published in 1944, was extremely important because, for the first time, scientists had proven that DNA controls the development of a cellular feature. It also implicated DNA as the basic genetic material of cells and stimulated James Watson and Francis Crick to later discover its structure and method of replication. Today we understand that DNA is the fundamental molecule involved in heredity. SEE ALSO WATSON, JAMES DEWEY.

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Avogadro, Amedeo

ITALIAN CHEMIST
1776–1856

atomic theory: physical concept that asserts that matter is composed of microscopically tiny particles called atoms and that various elements differ from each other by having different atoms

In 1811, just three years after John Dalton published his **atomic theory**, a brilliant theoretician named Amedeo Avogadro proposed his molecular theory. Avogadro's molecular theory related gas densities to molecular weights, explained reacting proportions by volume in terms of molecular ratios and compositions, and suggested methods for determining both molecular weights and compositions. His 1811 publication was a tour de force. Nonetheless, it was ignored for over half a century. Historians have sought reasons for the neglect of Avogadro's work in his life, his theory, and the state of chemistry at the time.

Avogadro's Life

Amedeo Avagadro was born in 1776 in Turin, a city in northwestern Italy. Avogadro spent his entire life within 80 kilometers (50 miles) of Turin, far from the cultural centers where chemistry was becoming a science. He received a classical education in the humanities, earned a doctorate in law in

1796 at the age of twenty, and practiced law for the next ten years. After auditing some courses and studying science on his own, Avogadro made a radical career change. In 1806 he became a secondary school science teacher, and in 1820 a university physics professor. He married in 1815, had seven children, and by all accounts, led a very happy family life.

During his academic career, Avogadro's publications revealed an intense curiosity, sharp intuition, vivid imagination, rigorous logic, and independent judgment—traits of an outstanding scientist. His obituary in an Italian scientific journal remarked on his retiring disposition and on the simplicity of his life, and it noted his other researches, but it did not mention the 1811 paper on his molecular theory.

Avogadro's Molecular Theory

Avogadro made two assumptions about molecules in his 1811 publication. The first assumption is now known as Avogadro's hypothesis, sometimes also called the EVEN hypothesis. It stated that equal volumes of gases contain equal numbers (thus, even) of molecules at the same temperature and pressure. The hypothesis was based on a model of the gas state in which molecules are far apart and equally spaced so that each molecule occupies the same volume. The second assumption was that gas molecules can divide during chemical reactions.

Avogadro used the EVEN hypothesis to interpret gas densities and assign molecular weights. EVEN implies that the density of a gas at a given temperature and pressure depends only on the weight of its molecules. Avogadro supposed that since the reported **gas density** of oxygen was 15 times that of hydrogen, the molecular weight of oxygen was 15 times that of hydrogen (the modern calculation of the ratio of the densities and molecular weights is actually sixteen). Consequently, he assigned oxygen a molecular weight of 15, relative to 1 for hydrogen. By this method Avogadro could determine a molecular weight for any gas, given its density.

gas density: weight in grams of a liter of gas

Avogadro needed both assumptions to explain reacting proportions and molecular compositions. For example, when water forms, the reacting proportions of hydrogen, oxygen, and water are 2:1:2 by volume. On the basis of the EVEN hypothesis, a 2:1:2 volumetric ratio should correspond to a 2:1:2 molecular ratio. Thus, two molecules of hydrogen (h) should combine with one molecule of oxygen (o) to give two molecules of water. Direct combination, however, would give only one molecule of h_2o. To fit the volumetric data, Avogadro split the h_2o water molecule into two $ho_{1/2}$ molecules. This in turn forced him to assume that oxygen molecules could divide into two "half molecules" during the reaction: $2h + o \rightarrow [h_2o] \rightarrow 2ho_{1/2}$. He expressed the composition of water as one "half molecule" of oxygen combined with one molecule of hydrogen ($ho_{1/2}$). With the aid of his two assumptions—EVEN and divisible molecules—Avogadro determined compositions for water, ammonia, hydrogen chloride, and gaseous oxides of nitrogen, carbon, and sulfur.

Early Nineteenth-Century Chemistry

The state of chemical theory and practice in 1811 was primitive by modern standards and not yet ready for Avogadro's molecular theory. Dalton's model of the gas state (atoms of different size in contact) precluded EVEN. Jöns Jakob Berzelius, another very influential chemist, believed gaseous elements like oxygen contained only indivisible atoms, not divisible molecules. Gas density and combining ratios data were limited and inaccurate. Atomic weights depended on unknown formulas and vice versa—a vicious cycle.

Conclusion

In retrospect the neglect of Avogadro's theory seems quite understandable. In 1811 he was a secondary school teacher living in a remote province. Furthermore, he was a theoretical physicist writing for practical chemists in legal language. His molecular theory was based on speculative assumptions, lacked independent experimental evidence or theoretical justification, and could only explain but not predict volumetric ratios. His molecular ratios ($2h + o \rightarrow 2ho_{1/2}$) were far removed from modern atomic ratios ($2H_2 + O_2 \rightarrow 2H_2O$) and did not solve the **atomic weight**–formula problem. Chemists in the early nineteenth century, however, needed more immediately productive theories and much more experimental information before Avogadro's theory could be truly useful. It took half a century of effort, the development of organic chemistry, and the ingenuity of another Italian, Stanislao Cannizzaro, to build a modern chemistry on the foundations laid by Avogadro. Nonetheless, as Nobel Prize winner Linus Pauling observed in a 1956 article in *Science*, Avogadro's work "forms the basis of the whole of theoretical chemistry" and is "one of the greatest contributions to chemistry that has ever been made." SEE ALSO Berzelius, Jöns Jakob; Cannizzaro, Stanislao; Dalton, John; Pauling, Linus.

atomic weight: weight of a single atom of an element in atomic mass units (AMU)

John D. Hostettler

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b

B_1, Vitamin ***See Thiamin.***

B_2, Vitamin ***See Riboflavin.***

Baekeland, Leo

AMERICAN CHEMIST AND INVENTOR
1863–1944

Born in St. Martens-Latem, Belgium, Leo Hendrick Baekeland was the son of a cobbler (Karel Baekeland) and a housemaid (Rosalia Merchie). He earned a B.S. in 1882 and a D.Sc.in 1884, with the highest honors, in organic chemistry from the University of Ghent. He joined the faculty at Ghent, which was then a leading center for the study of coal tar compounds. Interested in becoming an inventor, Baekeland used a traveling scholarship to visit the United States in 1889 (the year he married Celine Swart). His interest in photographic development brought him into contact with Richard Anthony of E. & H. T. Anthony and Company, who recruited Baekeland to join his American-based photographic company.

After two years Baekeland became an independent consultant, but he had little money and few prospects. Nevertheless, after experimenting with silver chloride emulsions, he developed a high-quality photographic printing paper, called Velox, sensitive enough to be used with artificial light. In 1899 the Eastman Kodak Company (located in Rochester, New York) bought the rights to Velox from Baekeland and his partner Leonard Jacobi for $750,000. This product represented a great leap forward in modern photographic technology.

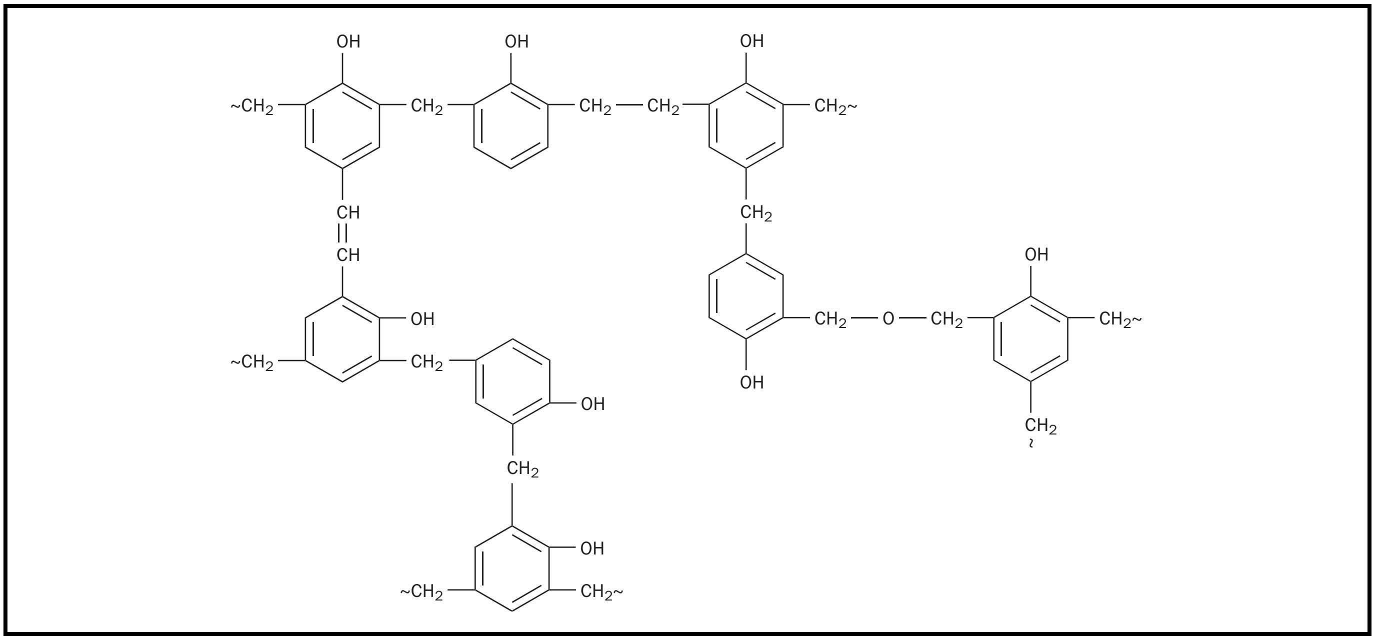

Figure 1. Structure of the phenol-formaldehyde polymer.

phenol: common name for hydroxybenzene (C_6H_5OH)

formaldehyde: name given to the simplest aldehyde, HC(O)H incorporating the −C(O)H functional group

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

catalyst: substance that aids in a reaction while retaining its own chemical identity

At his home laboratory in Yonkers, New York, Baekeland then returned to his early interest in resin chemistry. Reacting **phenol** and phenol derivatives with **formaldehyde**, he learned enough about controlling the **aldehyde**-phenol ratio with acids and alkalis to synthesize several resins. Most notable was the phenol-formaldehyde polymer resin (Figure 1) he produced with an alkali **catalyst**. Baekeland developed high pressure and high temperature techniques that greatly improved the molding of this plastic, which he named Bakelite and patented in 1909. It was a superhard, lightweight, insoluble plastic with a tensile strength of 7,000 pound force per square inch (psi). Baekeland claimed to have synthesized the first true plastic.

In 1910 Baekeland founded the General Bakelite Corporation in Perth Amboy, New Jersey, which began producing Bakelite on a commercial scale the following year. Bakelite was sold in liquid and powder form for molding to specifications. It quickly gained popularity in a variety of household and industrial uses—such as electrical insulation, billiard balls, tabletops, switchboards, and (later) automobile ignition systems—where it often replaced natural materials or earlier plastics, especially celluloid. By 1939 the factory was producing more than 50 million pounds of Bakelite a year. Baekeland and his firm controlled more than 400 patents. However, competition from major chemical companies was intensifying, and Baekeland's son George, who had worked for the company since 1923, did not wish to run it. So Baekeland, then seventy-five, sold the firm to Union Carbide and Carbon Corporation for roughly $16.5 million.

Baekeland earned many honors and awards, including the Franklin Medal of the Franklin Institute (1940), and the Perkin Medal (1916) and Messel Medal (1938) of the Society of the Chemical Industry. He was also elected president of the Chemists Club of New York (1904); the American Electrochemical Society (1909); the American Institute of Chemical Engineers (1912); and the American Chemical Society (1924). Eccentric in his old age, Baekeland spent much of his time alone, often in Coconut Grove, Florida, although he maintained a healthy correspondence with a number of colleagues on a broad range of subjects. He died in Beacon, New York, on February 23, 1944.

David B. Sicilia

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Bakelite ***See Baekeland, Leo.***

Balmer, Johann Jakob

SWISS MATHEMATICIAN
1825–1898

The name of Johann Jakob Balmer is immortalized in the Balmer series of **spectral lines** emitted from the hydrogen atom. Atoms that are excited to higher energies return to lower energies by emitting electromagnetic radiation at specific frequencies. Gustav Kirchhoff had shown in 1859 that each element has its own unique spectrum, but attempts to predict the frequencies of these spectral lines were unsuccessful until Balmer.

spectral line: line in a spectrum representing radiation of a single wavelength

After receiving a doctorate in mathematics from the University of Basel in Switzerland in 1849, Balmer taught at a girls' secondary school in Basel for the rest of his life; he was also a part-time university lecturer for many years. In 1885 he proposed an empirical formula for the wavelengths (l) of four hydrogen spectral lines in the visible region. The modern form of this equation is

$$\frac{1}{\lambda} = R\left(\frac{1}{n^2} - \frac{1}{m^2}\right)$$

where R is a constant. With the values $n = 2$, and $m = 3, 4, 5, 6$, the equation predicts the wavelengths of the four lines with considerable accuracy.

Aware of only these four lines, Balmer calculated l for a fifth line ($m = 7$). A line with a wavelength very close to the predicted value was observed experimentally. Balmer suggested that his formula might also predict wavelengths of other series of spectral lines by using integer values for n other than 2 and $m^3\ n + 1$. Other series of hydrogen lines were not known then, but were subsequently discovered (the Lyman, Paschen, Brackett, and Pfund series of lines).

There was no obvious reason why Balmer's formula should be so successful. Not until Niels Bohr proposed his atomic model in 1915 could line spectra be explained in terms of electrons moving from higher-energy orbits to lower-energy ones. SEE ALSO BOHR, NIELS.

Richard E. Rice

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Bardeen, John

AMERICAN PHYSICIST
1908–1991

In 1972 John Bardeen did something that no other physicist, not even Albert Einstein, had ever done. He won his second Nobel Prize in physics. The first was awarded to him (and to Walter H. Brattain and William Shockley) in 1956 for "investigations on semiconductors and the discovery of the transistor effect."

Their pioneering efforts ushered in the age of modern electronics and the integrated circuit, which eventually spawned the computer chip and the cell phone. Arguably, the transistor (and all of the devices it has made possible) is the single most important invention of this modern age and ranks with fire for its effects upon society and civilization.

Bardeen (along with Leon Neil Cooper and John Robert Schrieffer) won a second Nobel Prize in 1972 for "their jointly developed theory of superconductivity," usually called (using the last initials of the three scientists) the BCS theory. In essence, BCS theory explains the phenomenon of superconductivity in Type I superconductors—**metals**, such as mercury, lead, and niobium.

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

lattice: systematic geometrical arrangement of atomic-sized units that constitute the structure of a solid

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

According to BCS theory, at extremely low temperatures the **lattice** structures in these metals are very well-ordered and have little intrinsic vibrational motion. As an atom in a Type I superconductor gives up electrons to the **Fermi conduction levels**, it becomes a positively charged point in a sea of electrons. Below the critical temperature (the temperature at which a metal becomes superconducting), electrons in this Fermi level interact with the lattice atoms, producing vibrational motion that, in turn, interacts with a second electron. The result is the passage of electrons in the metal as "Cooper pairs," which move through the metal with zero resistance. Although Type I superconductors have not found extensive use because of their extremely low critical temperatures, the Type II or "alloy based" superconductors have radically changed science and technology, as they have enabled the construction of superconducting magnets, used in a range of devices, including magnetic resonance imaging (MRI) devices. SEE ALSO EINSTEIN, ALBERT; SUPERCONDUCTORS.

Todd W. Whitcombe

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Barium

MELTING POINT: 729°C
BOILING POINT: 1,640°C
DENSITY: 3.51 g/cm^3
MOST COMMON IONS: Ba^{2+}

56
Ba
BARIUM
137.33

The fifty-sixth element in the Periodic Table, barium has been known in various mineral forms since the 1600s. However, it was not until the 1770s that Carl W. Scheele and J. G. Gahn independently began separating barium compounds from other components of various minerals, isolating barium oxide (BaO) and barium sulfide ($BaSO_4$). The latter compound was isolated from the heavy feldspar and eventually named barite, from the Greek word *barys*, meaning "heavy." It was not until 1808 that elemental barium was isolated by Sir Humphry Davy, using his famous electrolysis system.

In its elemental form, barium is a relatively soft, silvery-white **metal**. As a highly reactive member of the alkaline-earth family, metallic barium will oxidize readily in water to form barium hydroxide, evolving hydrogen gas. It will also react readily and vigorously with oxygen in air to form BaO. As with other alkaline-earth elements, barium's most common **oxidation** state is +2.

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)

As the fourteenth most abundant element in Earth's crust, barium is the most common of all elements with an **atomic number** greater than 26 (iron). Barium and its compounds are used in a variety of ways, including in electronics, fireworks (where barium burns with its well-known yellow-green flame), paint pigments, and insecticides. Although barium compounds are highly toxic, doctors sometimes have patients ingest a special barium sulfate solution when it is necessary to x-ray their digestive tracts. The $BaSO_4$ is insoluble enough that it is not absorbed and so passes through the body without causing harm. In the process, the $BaSO_4$ can deflect X rays, thus making it possible to clearly image the soft tissue of the digestive tract. SEE ALSO ALKALINE EARTH METALS; DAVY, HUMPHRY; SCHEELE, CARL.

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

David A. Dobberpuhl

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Base Pairing

James Watson and Francis Crick proposed the molecular structure of deoxyribonucleic acid (**DNA**) in 1952. Gathering a number of experimental findings on DNA, including x-ray diffraction patterns of DNA fibers, they proposed that DNA was a double-stranded helical molecule, with its **hydrophobic** bases occupying the interior of the molecule, and its **hydrophilic**

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

hydrophobic: a part of a molecule that repels water

hydrophilic: a part of a molecule having an affinity for water

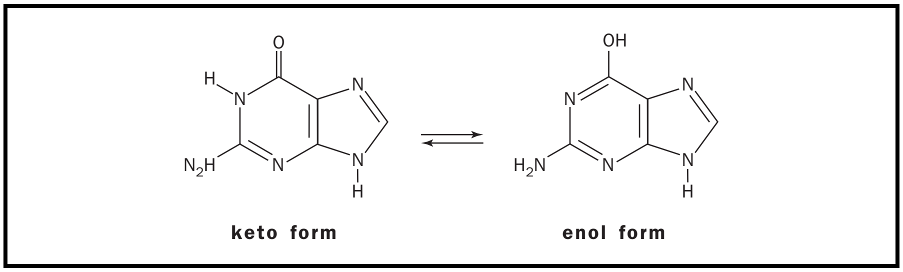

Figure 1. The tautomeric pair for guanine.

deoxyribose and phosphates groups occupying (or being oriented toward) the outer surfaces, interacting with water. The 20-angstrom (7.9×10^{-8}-inch) diameter of the **helix** was consistent with the presence of two adjacent strands and supported the hypothesis that a **purine base** resided on one strand and a **pyrimidine base** on the equivalent (homologous) site of the complementary strand.

Biochemist Erwin Chargaff had shown that the numbers of **adenine** and **thymine** units found in DNA were identical, and likewise for **guanine** and **cytosine** units. The ways in which the individual bases in the complementary A–T and G–C base pairs interacted to produce this one-to-one correspondence were not understood. The heterocyclic bases contain **functional groups**: ring nitrogens, carbonyl groups, and exocyclic amino groups that define much of the character of the bases. Interestingly, each base can occur in two structural forms, called *tautomers.* For example, the tautomeric pair that describes guanine, referred to as the *keto* and the *enol* forms, is shown in Figure 1. They are in **equilibrium**, with the keto form being favored by a factor of (approximately) 1,000 to 1. Once Watson and Crick had determined the correct tautomeric forms for each base, the nature of the phenomenon of pairing became clear.

A G–C base pair contains three specific **hydrogen bonds** within itself, whereas an A–T base pair contains two hydrogen bonds. (See Figure 2.) It is important to note that the presence of an incorrect tautomeric form in DNA would engender very different **hydrogen bonding** interactions, and the structural **complementarity** of base pairs would, in this instance, not exist. This simple yet elegant complementarity of the A–T and G–C base pairs also provides a mechanism to ensure that the proper bases are in-

helix: form of a spiral or coil such as a corkscrew

purine base: one of two types of nitrogen bases found in nucleic acids

pyrimidine base: one of two types of nitrogen bases found in nucleic acids

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

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

guanine: heterocyclic, purine, amine base found in DNA

cytosine: heterocyclic, pyrimidine, amine base found in DNA

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

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

hydrogen bond: interaction between H atoms and lone pair electrons that constitutes hydrogen bonding

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

complementarity: basis for copying the genetic information, where each nucleotide base has a complementary partner with which it forms a base pair

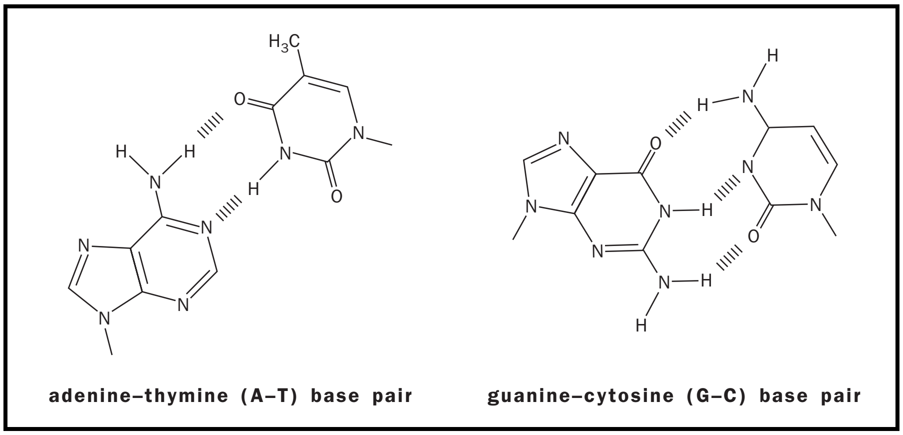

Figure 2. The complementary Watson-Crick base pairs, A–T and G–C.

corporated into DNA during DNA replication. SEE ALSO DNA REPLICATION; WATSON, JAMES DEWEY.

William M. Scovell

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Bases

Bases are considered the chemical opposite of acids because of their ability to neutralize acids. In 1887 the Swedish physicist and chemist Svante Arrhenius defined a base as the chemical substance that produces hydroxide ions (OH^-) and cations. A typical base, according to the Arrhenius definition, is sodium hydroxide (NaOH). The neutralization of an acid with a base to yield salt and water may be represented as

$$\mathrm{HCl}\ (aq) + \mathrm{KOH}\ (aq) \leftrightarrows \mathrm{H_2O}\ (l) + \mathrm{KCl}\ (aq) \qquad (1)$$

A major problem with Arrhenius's definition of bases is that several chemical compounds, such as $NaHCO_3$, Na_2CO_3, Na_3PO_4, which produce basic solutions when dissolved in water, do not contain hydroxide ions. The Brønsted-Lowry theory, which was proposed independently by Danish chemist Johannes Brønsted and English chemist Thomas Lowry in 1923, states that a base accepts hydrogen ions and an acid donates hydrogen ions. This theory not only includes all bases containing hydroxide ions, but also covers any chemical species that are able to accept hydrogen ions in **aqueous solution**. For example, when sodium carbonate is dissolved in solution, the carbonate ion accepts a hydrogen ion from water to form the bicarbonate ion and hydroxide ion.

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

$$\underset{\text{base}}{\mathrm{CO_3}^{2-}\ (aq)} + \underset{\text{acid}}{\mathrm{H_2O}\ (l)} \leftrightarrows \underset{\text{conjugate acid}}{\mathrm{HCO_3}^{-}\ (aq)} + \underset{\text{conjugate base}}{\mathrm{OH}^{-}\ (aq)} \qquad (2)$$

The Brønsted-Lowry theory includes water as a reactant and considers its acidity or basicity. In reaction (2) a new acid and base are formed, which are called the conjugate acid and conjugate base, respectively.

The strength of a base is determined by the extent of its **ionization** in aqueous solution. Strong bases, such as NaOH, are 100 percent ionized in aqueous solution and weak bases, such as ammonia, are only partially ionized in aqueous solution.

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

$$\underset{\text{base}}{\mathrm{NH_3}\ (aq)} + \underset{\text{acid}}{\mathrm{H_2O}\ (l)} \leftrightarrows \underset{\text{conjugate acid}}{\mathrm{NH_4}^{+}\ (aq)} + \underset{\text{conjugate base}}{\mathrm{OH}^{-}\ (aq)} \qquad (3)$$

The partial ionization is a dynamic **equilibrium**, as indicated by the double arrow in equation (3).

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

The strength of acids and bases also determines the strength of their conjugate bases and conjugate acids, respectively. Weak acids and bases have strong conjugate bases and acids. For example, when ammonium chloride is dissolved in water, it gives an acidic solution because ammonium ion is a strong conjugate acid of the weak base ammonia, but chloride ion is a weak conjugate base of the strong acid hydrochloric acid.

$$NH_4^+ \ (aq) + H_2O \ (l) \rightarrow NH_3 \ (aq) + H_3O^+ \ (aq) \qquad (4)$$

The carbonate ion in equation (2) yields a basic solution because it is the strong conjugate base of the weak acid HCO_3^-.

When $NaHCO_3$ is dissolved in water, it gives a basic solution, even though a hydrogen ion is available. Predicting this requires one to consider the strength of carbonic acid, H_2CO_3, which is a very weak acid.

$$H_2CO_3 \ (aq) + H_2O \ (l) \leftrightarrows HCO_3^- \ (aq) + H_3O^+ \ (aq) \qquad (5)$$

However, HCO_3^- will act as an acid if a strong base is added.

$$HCO_3^- \ (aq) + OH^- \ (aq) \rightarrow H_2O \ (l) + CO_3^{2-} \ (aq) \qquad (6)$$

anion: negatively charged chemical unit, like Cl^-, CO_{32}^-, or NO_3^-

This ability to act as a base or an acid is called amphoterism. Any **anions** of polyprotic acids, such as HCO_3^-, $H_2PO_4^-$, and HPO_4^{2-}, which contain replaceable hydrogen ions, are amphoteric. Some hydroxides, such as $Al(OH)_3$ and $Zn(OH)_2$, are also amphoteric, reacting with a base or acid, as illustrated by the following equations:

$$Al(OH)_3 \ (s) + OH^- \ (aq) \rightarrow Al(OH)_4^- \ (aq) \qquad (7)$$

$$Al(OH)_3 \ (s) + 3 \ H_3O^+ \ (aq) \rightarrow Al^{3+} \ (aq) + 6 \ H_2O \ (l) \qquad (8)$$

Equations (7) and (8) can also be explained by American chemist Gilbert Lewis's acid-base theory. A Lewis acid is a substance that can accept a pair of electrons to form a new bond, and a Lewis base is a substance that can donate a pair of electrons to form a new bond.

$$\underset{\text{acid}}{A} + \underset{\text{base}}{:B} \rightarrow \underset{\text{adduct}}{A\text{—}B} \qquad (9)$$

metal cation: positively charged ion resulting from the loss of one or more valence electrons

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

All Arrhenius and Brønsted-Lowry bases are also Lewis bases. All **metal cations** are potential Lewis acids. Complexes of **metal** ions with water, ammonia, and hydroxide ion are examples of Lewis acid-base reactions. For example, $[Al(H_2O)_6]^{3+}$ may be regarded as a combination of the Lewis acid, Al^{3+}, with six electron pairs from six H_2O molecules.

Buffer solutions contain a base and an acid that can react with an added acid or base, respectively, and they maintain a pH very close to the original value. Buffers usually consist of approximately equal quantities of a weak acid and its conjugate base, or a weak base and its conjugate acid. For example, one of the buffers used to keep the pH of the blood near 7.45 is the $H_2PO_4^-/HPO_4^{2-}$ acid/conjugate base system. Small amounts of an acid or base react with one of the components of the buffer mixture to produce the other component as follows:

$$H_2PO_4^- \ (aq) + OH^- \ (aq) \rightarrow H_2O \ (l) + HPO_4^{2-} \ (aq) \qquad (10)$$

$$HPO_4^{2-} \ (aq) + H_3O^+ \ (aq) \rightarrow H_2O \ (l) + H_2PO_4^- \ (aq) \qquad (11)$$

SEE ALSO Acid-Base Chemistry; Arrhenius, Svante; Brønsted, Johannes Nicolaus; Chemical Reactions; Lewis, Gilbert N.; Solution Chemistry.

Melvin D. Joesten

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Batteries *See New Battery Technology.*

Becquerel, Antoine-Henri

FRENCH PHYSICIST
1852–1908

Antoine-Henri Becquerel was born the son of the physicist Alexandre-Edmond Becquerel, and the grandson of the physicist Antoine-César Becquerel, and it is not surprising that he followed in their footsteps. It is also not surprising that his research interests centered around solar radiation and phosphorescence, as these are phenomena that his father had investigated. He entered the École Polytechnique, in Paris, in 1872, which he left in 1874 and to which he subsequently returned. Becquerel received a doctorate degree from the Faculty of Sciences of Paris in 1888. In 1892, he was appointed professor of applied physics in the Department of Natural History at the Paris Museum, and in 1895, professor of physics at the École Polytechnique.

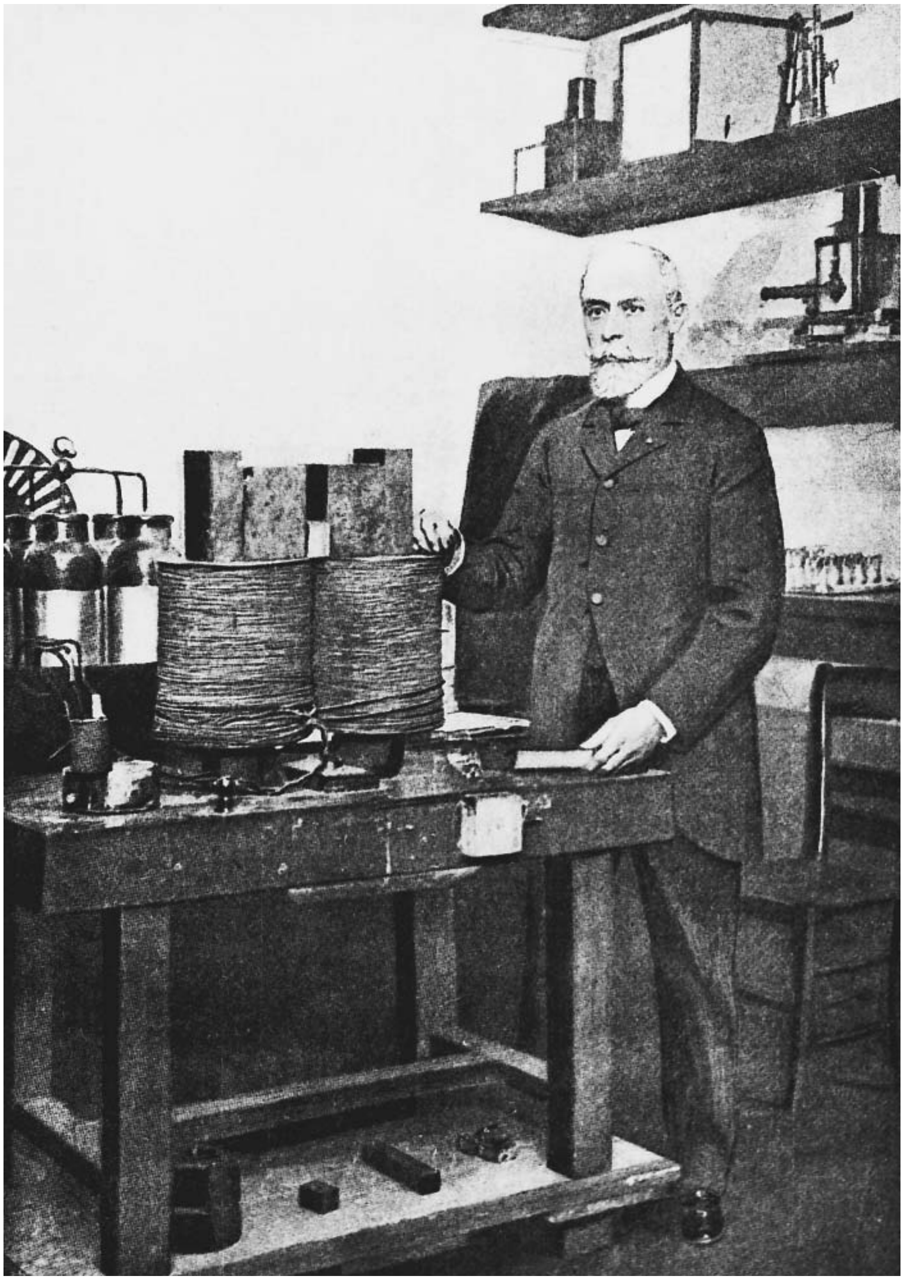
Becquerel's early work focused on plane-polarized light, the phenomenon of phosphorescence (in which certain compounds glow after being exposed to direct light), and the absorption of light by crystals. But all of his early research became overshadowed by his discovery of natural radioactivity. Although Becquerel did not initially comprehend what he was observing, his landmark discovery of radioactivity paved the way for a new understanding of the atom and atomic structure.

On February 24, 1896, Becquerel attended a meeting of the French Academy of Science and presented a short paper (one of the quickest methods in France at that time for disseminating results). One can well imagine Becquerel's excitement as he reported his results to the members of the academy.

> One wraps a Lumiere photographic plate with a bromide **emulsion** in two sheets of very thick black paper, such that the plate does not become clouded upon being exposed to the Sun for a day. One places on the sheet of paper, on the outside, a slab of the phosphorescent substance, and one exposes the whole to the Sun for several hours. When one then develops the photographic plate, one recognizes that the silhouette of the phosphorescent substance appears in black on the negative. (Becquerel *Comptes Rendus*)

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

From this simple experiment, Becquerel concluded that the phosphorescent substance had to be emitting a type of ray that was passing through the paper and reducing the silver in the emulsion. This would seem to make sense, as the production of X rays, discovered a few years earlier by Wilhelm Röntgen, is accompanied by a soft glowing spot at the surface of the cathode ray tube. Becquerel decided to probe his unusual rays a little further. One week later, on March 2, 1896, Becquerel was back before the French Academy with the results of his further experiments. He had continued his experiments using a double sulfate salt of uranium and potassium



French physicist Antoine-Henri Becquerel, co-recipient of the 1903 Nobel Prize in physics, “in recognition of the extraordinary services he has rendered by his discovery of spontaneous radioactivity.”

(potassium uranium sulfate monohydrate), which has a strong but short-lived phosphorescence.

He carefully wrapped his photographic plates in black paper, coating the paper with a crust of the uranium double salt, and upon exposure to sunlight he once again observed the “signature” of the phosphorescence-induced rays. However, repeating the experiment on Wednesday, February 26, and Thursday, February 27, he was frustrated by two days of only intermittent sunlight. And because the Sun made no appearance on the two days following, on March 1 he developed his plates. Expecting to see only a faint silhouette resulting from the wrapped plates’ intermittent exposure to sunlight, he was surprised to see that the silhouettes appeared with great intensity.

Becquerel suspected that the rays that produced the silhouettes emanated from the uranium salt itself, and that the small amount of sunlight was of no consequence. He arranged three more experiments, in which photographic plates were kept completely in the dark but put in direct contact with: (1) the salt; (2) a thin sheet of glass; and (3) a thin sheet of aluminum. He surmised that the glass would eliminate any possibility that a silhouette was the consequence of a chemical reaction, and that the aluminum would block the mysterious rays.

Developing the photographic plates, Becquerel observed an intensely defined silhouette on the first two plates, and a clear but considerably weaker silhouette on the third. Because he had double-boxed his plates inside his dark room and had placed the ensembles inside a drawer that he then closed, he was able to conclude that his mysterious rays were not related to phosphorescence and were not induced by sunlight.

It was another four years before Becquerel's radiation became understood as the production of β-rays (high energy electrons), but by then there was no question that Becquerel had discovered the instability of some atomic nuclei, and that he was richly deserving of the 1903 Nobel Prize that he shared with Pierre and Marie Curie. SEE ALSO CURIE, MARIE SKLODOWSKA; RÖNTGEN, WILHELM.

Todd W. Whitcombe

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Berg, Paul

AMERICAN BIOCHEMIST
1926–

Paul Berg is considered to be one of the few pioneers in molecular biology, which is essentially the application of chemistry to biological systems. His work with recombinant DNA provided scientists with a very valuable laboratory technique. Berg worked with cloning genes from two different organisms. These hybrid DNA molecules could be produced in larger amounts and the DNA sequence could then be determined. It was also possible to change the genes and put them back into the cells from which they were obtained to determine the effects these specific changes would have on the gene function. Genes from one organism, such as a bacterium, virus, or yeast cell, could be introduced into the cells of another simple organism by the same technique, thus adding new functions to organisms. Later, microorganisms were developed that would synthesize compounds useful in research, commerce, and medicine. Today, insulin and factor VIII are two common drugs produced by recombinant organisms that help treat diabetes and hemophilia, respectively. Bacteria that feed on oil have been designed to assist in cleaning up oil spills. The applications are endless.

Berg understood the darker side of this technology too. He knew that it was theoretically possible to create new organisms with new pathogenic abilities which may be able to infect humans with new diseases. These diseases could be potentially deadly since the body would not have a chance to build up any immunity against them. In 1975, Berg and others working in recombinant DNA technology recommended a set of regulations, known as the "Berg Letter" to prevent such problems. These research guidelines are still in place today, although some rules have been relaxed as control over such experimentation has increased.

Dr. Berg's interest in science began early. He graduated from Pennsylvania State University in 1948 and obtained his doctorate from Case Western Reserve University in 1952. He spent several years as a research fellow at the Institute of Cytophysiology in Denmark and later at Washington University in St. Louis, Missouri. He was eventually promoted to chairman of the microbiology department at Washington University. By 1959, Berg moved west to Stanford University where he served as professor of biochemistry. In February of 1975 he helped organize the Asilomar Conference, an international forum on advances in DNA technology. Paul Berg has earned many prestigious awards and honors, including election into the American Academy of Arts and Sciences and the National Academy of Sciences. Perhaps the highlight of his career came in 1980 when he shared the Nobel Prize in chemistry with Walter Gilbert and Frederick Sanger for his work with DNA. SEE ALSO Genes; Genetic Engineering; Recombinant DNA.

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Berkelium

97
Bk
BERKELIUM
247

MELTING POINT: 986°C
BOILING POINT: Unknown
DENSITY: Unknown
MOST COMMON IONS: Bk^{3+}, Bk^{4+}

Berkelium, element 97, is a synthetic **radioelement**, first synthesized by Glenn Seaborg's group in 1949. A target of a few milligrams of an **isotope** of americium (^{241}Am) was bombarded with **α-particles** within a cyclotron at the University of California at Berkeley. An α-emitting species with a half-life of 4.5 hours was isolated via **ion exchange chromatography** and identified as being an isotope of element 97 with mass number 243. The first isolation of a berkelium compound was accomplished by Stanley Thompson and B. B. Cunningham in 1958. The known isotopes of berke-

radioelement: a radioactive element; one in which the nucleus spontaneously decomposes (decays) producing α (alpha) and β (beta) particles and gamma rays

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; an He nucleus

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 lium have mass numbers that range from 240 to 251, and are all radioactive. The longest-lived isotope has a mass number of 247 and a half-life of 1,380 years. The ground state electronic configuration of the outer orbitals of berkelium is $5f^8 6d^1 7s^2$. In compounds and in **aqueous solution**, berkelium is present in **oxidation** states III (the more stable) and IV.

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

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

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

Berkelium was named for the city in which it was discovered, in part to emphasize its relationship to its analog in the **lanthanide** series, terbium, which was named for the city of Ytterby in Sweden (where many of the rare earth minerals had been discovered). Metallic berkelium has a face-centered cubic structure—something it has in common with the actinide elements americium though einsteinium. Due to the very high level of radioactivity of even the long-lived isotopes, berkelium is usually studied at tracer level concentrations. The most commonly studied isotope is ^{249}Bk, with a half-life of 320 days. This nuclide has been isolated at milligram levels and undergoes β-decay. SEE ALSO ACTINIUM; EINSTEINIUM; FERMIUM; LAWRENCIUM; MENDELEVIUM; NEPTUNIUM; NOBELIUM; PLUTONIUM; PROTACTINIUM; RUTHERFORDIUM; SEABORG, GLENN THEODORE; THORIUM; URANIUM.

Gregory R. Choppin

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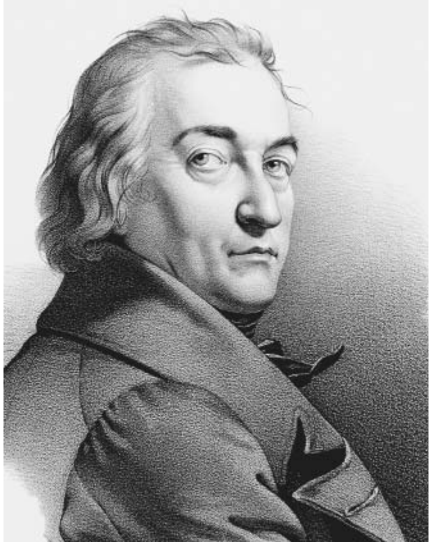
Berthollet, Claude-Louis

FRENCH CHEMIST
1748–1822



French chemist Claude-Louis Berthollet, developer of a chlorine-based bleach.

Claude-Louis Berthollet was influential in four areas: theoretical chemistry, experimental chemistry, practical chemistry, and chemical writing. He was also a chemistry teacher and, with his contemporary Pierre-Simon de Laplace, a patron of young French scientists. Born in 1748 in the town of Talloire, near Annecy, France, Berthollet studied medicine at the University of Turin. Arriving in Paris in 1772, he soon found a medical patron in one of the great Parisian aristocrats, Louis-Philippe, duke of Orléans. To consolidate his professional status, Berthollet obtained a medical degree at the University of Paris and continued to practice medicine until the mid-1780s. During the 1770s he had acquired an active interest in chemistry. By 1780 he had presented eighteen mémoires to the Académie des Sciences. He was admitted to the Académie as an *adjoint* in 1780, promoted to *associé* in 1785, and promoted to its highest position, *pensionnaire*, in 1792.

By the early 1780s, Berthollet had gained entrance to the circle of chemists that surrounded Antoine-Laurent Lavoisier, who had been developing his new oxygen-based, antiphlogistic theory of chemistry. Although Berthollet at first criticized features of the new chemistry (and never did accept Lavoisier's oxygen-based theory of acidification), he was the first chemist of Lavoisier's circle to formally and publicly become a supporter. In 1787 he joined with Lavoisier's other close associates (including Antoine

Fourcroy and Louis-Bernard Guyton de Morveau) to forge a chemical nomenclature that would be coordinated with the new chemistry.

In 1784 Berthollet was appointed to the post of inspector of the dye works and director of manufacture at the Gobelin tapestry works. While studying the properties of newly discovered chlorine gas ("dephlogisticated marine acid"), Berthollet recognized its superior bleaching properties, and he developed a chlorine-based bleach. In 1791 Berthollet published *Élémens de l'art de la teinture*, a systematic study and scientific discussion of the nature of dyeing. Berthollet also contributed to another scientific study of a major industry of the 1780s: ironmaking and steelmaking. In this study an attempt was made to provide a scientific explanation of the different kinds of iron (cast, wrought) and steel based on degrees of reduction (removal of oxygen) of the ore and subsequent combination with carbon. A third area of practical chemistry in which Berthollet was active was munitions. His most significant work in this area was the development of a potassium chlorate–based explosive (which turned out to be too powerful for use as a munition).

During the French Revolution and the Napoleonic era, Berthollet came to play active civic and political roles in France. During the Revolution, he was one of the scientists entrusted by the Committee of Public Safety with the emergency amplification of munitions production. He taught at the École Normale and was one of the founders of the École Polytechnique. He became a friend of Napoleon Bonaparte, whom he accompanied to Egypt in 1798, and in Egypt helped to set up a scientific institute along the lines of the Parisian *Académie.* Under the aegis of Napoleon, Berthollet was made a count, a senator of Montpellier, and a *grand officier* of the Légion d'Honneur.

Although Berthollet never published a textbook of chemistry, he did publish the *Essai de statique chimique* (1803), an ambitious work that attempted to provide a systematic theoretical foundation for chemistry. Like his predecessors, Berthollet conceived of the microscopic-level forces by which chemical substances "attracted" one another as being the same as or analogous to gravity. But Berthollet challenged his predecessors' view that the strengths of chemical affinity forces were determined solely by the nature of the reagents and were invariant under all physical and chemical condition. He held that factors such as the masses of the reagents, their physical states before and after the reaction, and general physical circumstances could affect the directions of reactions and even the combining proportions of their products.

Regarding combining proportions, Berthollet asserted that chemical reagents in continuous ranges of weight proportions could combine, depending on the masses of the reagents and the physical circumstances of the reactions. By this time, Joseph-Louis Proust had already set forth his general assertion that true chemical combination was always marked by fixed-weight proportions of the reagents. Berthollet and Proust argued the issue in print for several years without any resolution of the argument. What "settled" the issue was the ascendancy of John Dalton's chemical atomic theory (1808), which in its laws of definite and multiple proportions supported Proust's position. SEE ALSO DALTON, JOHN; LAVOISIER, ANTOINE.

Seymour Mauskopf

Beryllium

4
Be
BERYLLIUM
9.0121

MELTING POINT: 1,285°C
BOILING POINT: 2,500°C
DENSITY: 1.848 g/cm^3
MOST COMMON IONS: Be^{2+}

Beryllium was identified as a unique element and as a constituent of the mineral beryl and the gem emerald by the French chemist Louis Vauquelin in 1797. Metallic beryllium was isolated in 1828 by the scientists (working independently of one another) Antoine Bussy and Friedrich Wöhler. Beryllium usage was not common until a 1920s discovery that the 2 percent addition of beryllium to copper resulted in an **alloy** six times stronger than the original material. Beryllium has a melting point of 1,285°C (2,345°F), a boiling point of 2,500°C (4,532°F), and a density of 1.848 g/cm^3. Its most common **oxidation** state is +2. It has a high heat adsorption capacity and is nonmagnetic and corrosion-resistant.

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

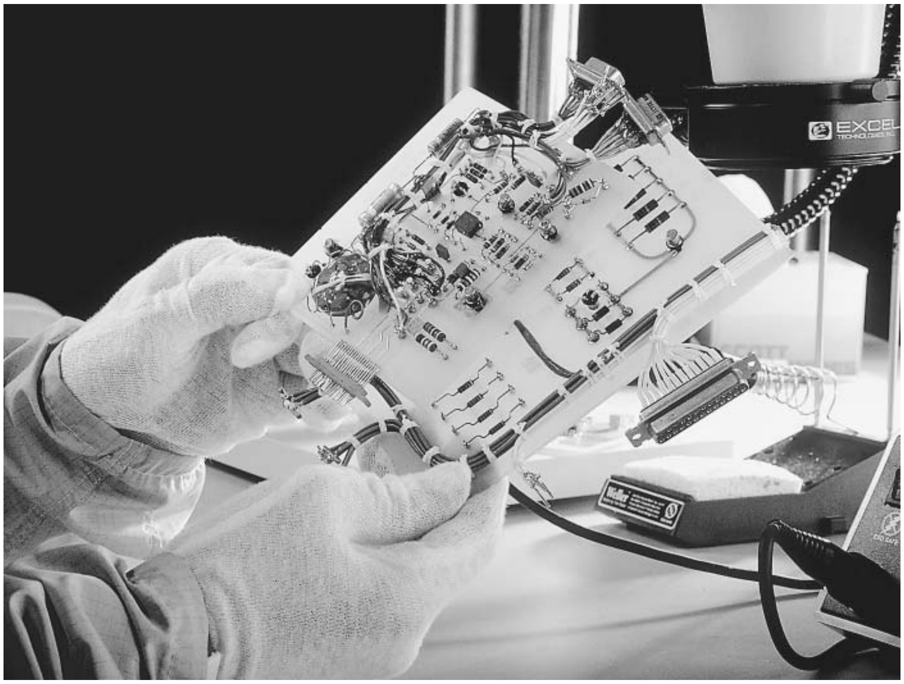
oxidation: process that involves the loss of electrons (or the addition of an oxygen atom)

Beryllium is one of the most toxic elements in the Periodic Table. It is the agent responsible for chronic beryllium disease (CBD), an often-fatal lung disease, and is a Class A carcinogen (as determined by the U.S. Environmental Protection Agency). The primary route of human exposure to beryllium and beryllium compounds is inhalation.

Approximately fifty beryllium minerals occur in nature and over half of these minerals are silicates. Beryllium is mined primarily from these silicates, including beryl, $Al_2Be_3Si_6O_{18}$, 5 percent (wt.) beryllium, and bertrandite, $Be_4(OH)_2Si_2O_7$, 15 percent (wt.) beryllium. The world resources of beryllium are estimated at approximately 80,000 tons. Other common beryllium silicates include chrysoberyl, $BeAl_2O_4$, and phenacite, Be_2SiO_4.

Beryllium is a key component of materials used in the aerospace, electronics, aviation, telecommunications, automotive, and **nuclear** power

nuclear: having to do with the nucleus of an atom



Circuit board assembly for a satellite transmitter. Beryllium is mined for the silicate beryl, which is used in aerospace electronics due to its high thermal conductivity.

industries. It is used in aircraft bearings and bushings; fuel containers for solid propulsion jet and rocket fuel systems; gyros, reentry vehicles, springs, switches, and relays and connectors in electronic systems; fiber optics and cellular network communication systems; optical laser scanners; automobile air bag sensors, ignition switches, and power steering systems; and to moderate nuclear reactions in power plants. Beryllium oxide ceramics have a thermal conductivity second only to that of diamond among electrically insulating materials, dissipating nearly 300 watts/millikelvin (W/mK) at room temperature. SEE ALSO TOXICITY; WÖHLER, FRIEDRICH.

Tammy P. Taylor
Nancy N. Sauer

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Berzelius, Jöns Jakob

SWEDISH CHEMIST
1779–1848

Before the early 1800s the symbols used to denote chemical elements and compounds were obscure. Alchemists wanted to keep their work secret and so devised symbols for the chemicals they used that would not reveal anything about them. This all changed with the work of Jöns Jakob Berzelius.

Berzelius was born in Linköping, Sweden, in 1779. Both of his parents died while he was young, yet he still managed to finance his education by tutoring. He became interested in nature at school, and while he was a medical student at the University of Uppsala, his interests became more focused on experimental chemistry. Berzelius was so taken with experimental work, he bribed a caretaker in order to gain extra access to the university's laboratory.

In addition to devising a new language of chemistry, Berzelius was also keenly interested in the analysis of minerals. In 1800 Berzelius was apprenticed to a physician at the Medivi mineral springs in Sweden. Here, he analyzed the mineral content of the spring water. It was while working at Medivi that he developed his quantitative analysis skills.

Berzelius's analytical skills were put to the test when he and a colleague, Johan Gottlieb Gahn (1745–1818), noticed a residual substance while studying a method of producing sulfuric acid in 1817. They at first thought the substance was tellurium, but after careful quantitative analysis, they realized that they had isolated a new element. They named this element selenium.

The most notable of Berzelius's contributions to chemistry was his development of a rational system of atomic symbols. Around 1810 Berzelius was working to confirm John Dalton's **atomic theory** as well as Proust's

atomic theory: physical concept that asserts that matter is composed of microscopically tiny particles called atoms and that various elements differ from each other by having different atoms law showing that separate elements always combined in whole-number proportions. At the same time, he was also compiling the new Swedish *Pharmacopoeia*. While working on these three projects, Berzelius came to the conclusion that the existing system of denoting elements and compounds was a hindrance. In establishing his own atomic symbols, he stated that "it is easier to write an abbreviated word than to draw a figure which has little analogy with words" (Jaffe 108). Instead of using obscure symbols like circles with arrows extending from their sides, or collections of dots arranged in a specific pattern, Berzelius opted to use the first letter of the Latin name for each element as its symbol. For example, carbon would be denoted as C and oxygen as O. If elements had the same first letter, such as gold (*aurum*) and silver (*argentum*), Berzelius decided that the symbol would be the first two letters of the name: Thus, gold would be known as Au and silver as Ag.

Berzelius then extended his development to represent compounds, for example, copper oxide was identified as CuO and zinc sulfide as ZnS. And, conforming to Proust's law and Dalton's theory, Berzelius added algebraic exponents (later to become subscripts) to his system of atomic symbols—for example, water was denoted as H_2O and carbon dioxide as CO_2.

Even though his atomic symbols were introduced in 1814, it was quite a few years before Berzelius's symbols were adopted by the chemistry community. But once accepted, they became the new international language of chemistry.

Berzelius published more than 250 papers in his lifetime covering every aspect of chemistry. He was devoted to the entire field of chemistry, as can be seen by his efforts to bring order to the language of chemistry and to insist on quantitative excellence in all its areas. He died in 1848 and is buried in Stockholm, Sweden. SEE ALSO ATOMS; DALTON, JOHN.

Lydia S. Scratch

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Bioluminescence

Bioluminescence is the emission of visible light by biological systems, which arises from enzyme-catalyzed chemical reactions. Bioluminescence can be distinguished from chemiluminescence in that it occurs in living organisms and requires an enzyme **catalyst**. These chemical-dependent emissions of light differ from fluorescence and phosphorescence, which involve the absorption of light by a compound followed by emission of light at a lower energy (higher wavelength) from the excited state of the molecule. The excited molecule produced during bioluminescence reactions, however, is

catalyst: substance that aids in a reaction while retaining its own chemical identity

The jellyfish is among many bioluminescent species.

analogous to that produced during fluorescence, and consequently the luminescence emission spectrum can often be related to the fluorescence emission spectrum. It should also be noted that the processes of fluorescence and phosphorescence also occur in living organisms and should not be confused with bioluminescence.

Bioluminescence has been observed in many organisms and phyla throughout the terrestrial and aquatic worlds, with the majority of luminescent organisms being found in the ocean. Because of the ease with which light can be detected, recorded observations of bioluminescence extend back several thousand years. Both the ancient Chinese and the ancient Greeks recorded luminescence sightings. Aristotle, in the fourth century B.C.E., wrote that "some things, though they are not in their nature fire, nor any species of fire, yet seem to produce light."

Luminescent species are found among marine and terrestrial bacteria, annelids or segmented worms (e.g., fireworms), beetles (e.g., fireflies, click beetles, railroad worms), algae (e.g., dinoflagellates), crustaceans (e.g., shrimp, ostracod), mollusks (e.g., squid, clams, limpets), coelenterates (e.g., jellyfish, sea pansies, hydroids), bony fish (e.g., hatchet fish, flashlight fish, pony fish), and cartilaginous fish (e.g., sharks). Luminescent vertebrates (except for certain fish), mammals, higher plants, and viruses do not exist—except for those versions created by recombinant technology.

Most, if not all, bioluminescence reactions have oxygen as a common reactant and a conjugated system as part of one of the substrates—both needed to generate molecules in an excited state, leading to the emission of light in the visible region. However, the bioluminescence reactions in some organisms are quite different from those in other organisms, and consequently the enzymes catalyzing the reactions (luciferases) and the substrates (often but not always referred to as luciferins) are also quite

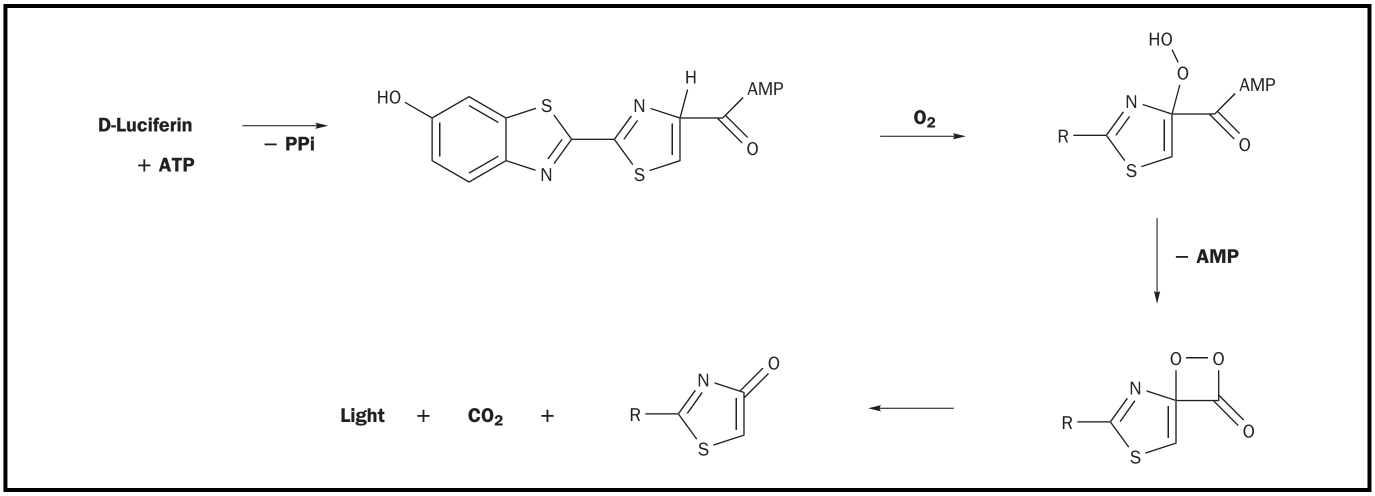


Figure 1. Bioluminescence reaction in fireflies.

distinct. Four bioluminescence systems (fireflies, dinoflagellates, bacteria, and imidazolopyrazine-based e. g., coelenterates) have been studied in greatest detail, and their chemical reactions reflect both their differences and their common features.

Beetles/Fireflies

Luciferases from click beetles, fireflies, and railway worms catalyze the ATP-dependent decarboxylation of luciferin (Figure 1). An AMP derivative of luciferin is formed, which subsequently reacts with O_2. Cleavage of this dioxy derivative results in the emission of light characterized by wavelengths ranging from 550 nanometers (2.17×10^{-5} inches; green) to 630 nanometers (2.48×10^{-5}; red, depending on the particular luciferase), and the release of CO_2. Fireflies generally emit in the yellow to green range, as part of a courtship process; click beetles emit green to orange light; whereas railway worms emit red light, with green light being emitted on movement.

Dinoflagellates

Much of the brightness that is observed on the surface of the oceans is due to the bioluminescence of certain species of dinoflagellates, or unicellular algae, and this bioluminescence accounts for many of the recorded observations that have described the apparent "phosphorescence" of the sea. Dinoflagellates are very sensitive to motion induced by ships or fish, and respond with rapid and brilliant flashes, thus causing the glow that is sometimes seen in the wake of a ship. The luciferin in these instances is a tetrapyrrole containing four five-member rings of one nitrogen and four carbons, and its **oxidation**, catalyzed by dinoflagellate luciferase, results in blue-green light centered at about 470 nanometers (1.85×10^{-5} inches; Figure 2).

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

Bacteria

Bacterial luciferase catalyzes the reaction of reduced flavin mononucleotide ($FMNH_2$) with O_2 to form a 4a-peroxyflavin derivative that reacts with a

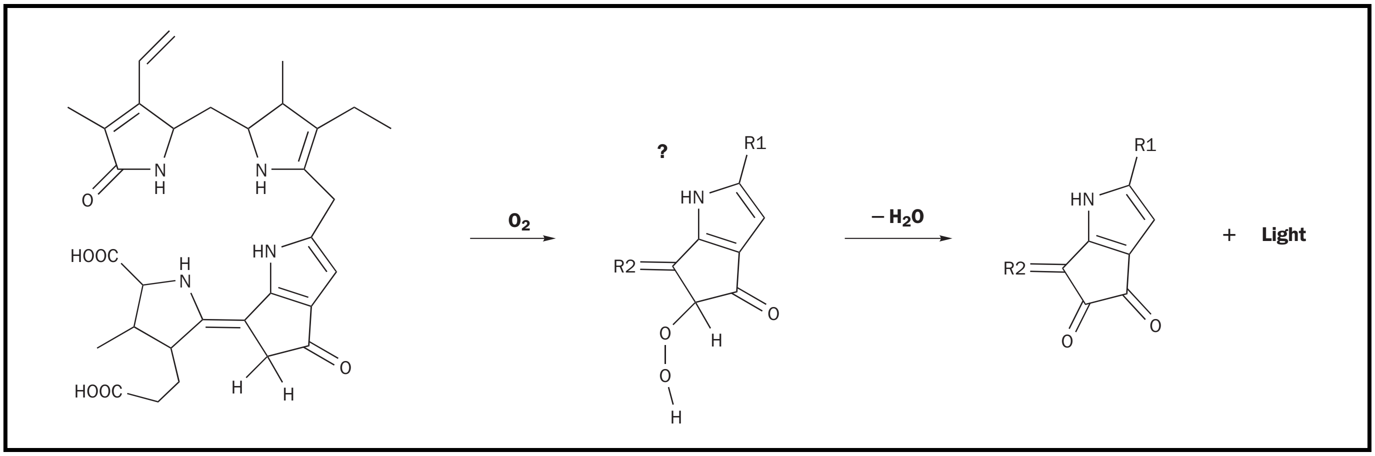


Figure 2. Bioluminescence reaction in dinoflagellates.

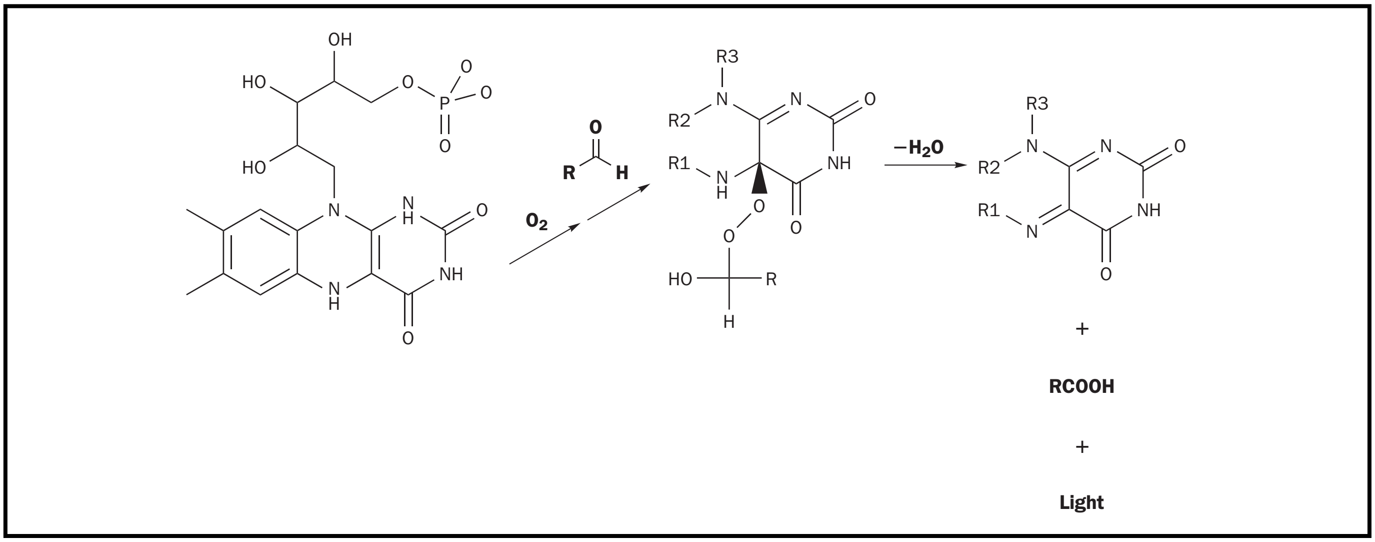
aldehyde: one of the characteristic groups of atoms in organic compounds that undergoes characteristic reactions, generally irrespective of where it occurs in the molecule; the RC(O)H functional group

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

long chain **aldehyde** leading to the emission of blue-green light (490 nanometers, or 1.93×10^{-5} inches) and the formation of riboflavin phosphate (FMN; the phosphorylated form of **vitamin** B_2), H_2O, and the corresponding fatty acid (Figure 3). Luminescent bacteria are found throughout the marine environment, living free, in symbiosis, or in the gut of marine organisms (including many fish and squid), as well as in the terrestrial environment as symbionts of nematodes.

The luciferins believed to be the most widespread among phyla living in the ocean have structures based on imidazolopyrazine, for example, coelenterazine, found in luminescent coelenterates contains imidazolopyrazine as its central bicyclic ring (Figure 4). The typical reaction involves the oxidation of the imidazolopyrazine ring with the emission of blue light (460–480 nanometers, or 1.81×10^{-5}–1.89×10^{-5} inches), and proceeds according to a mechanism that is very similar to that of the oxidation of firefly luciferin. Among the most commonly studied imidazolopyrazine-utilizing organisms are species of *Renilla* (sea pansy) and *Aequorea* (jellyfish) both of which utilize coelenterazine. The luciferin of a crustacean (*Cypridina* or

Figure 3. Bioluminescence reaction in bacteria.



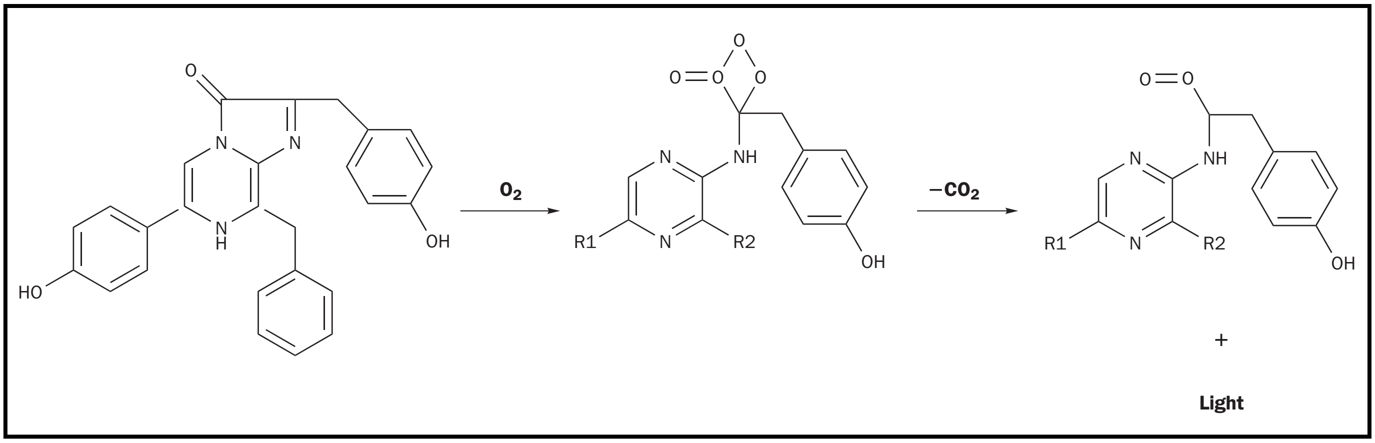


Figure 4. Bioluminescence reaction in coelenterates.

Vargula) also is an imidazolopyrazine-based compound related to coelenterazine. The luciferases of the luminescent species, however, vary widely. Recent evidence suggests that some, and possibly many, marine luminescent organisms (including the jellyfish) acquire luciferins via the ingestion of other luminescent organisms, which would account for the widespread distribution of imidazolopyrazine-based luciferins. Many luminescent species also have a binding protein that releases the luciferin upon Ca^{++} uptake, while some have a fluorescence protein that absorbs and then emits light at a higher wavelength.

Although other luminescent systems have been studied (including those of the fireworm and the limpet, both of which use aldehydes as luciferins), bioluminescence remains somewhat mysterious. Elucidation of the chemical and biological bases for luminescence systems in other organisms should improve understanding of why the remarkable and beautiful phenomenon of bioluminescence appears in so many species. SEE ALSO CHEMILUMINESCENCE.

Edward A. Meighen

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83
Bi
BISMUTH
208.9804

Bismuth

MELTING POINT: 271.4°C
BOILING POINT: 1,564 ±5°C
DENSITY: 9.747 g/cm^3
MOST COMMON IONS: Bi^{3+}, Bi^{4+}

Bismuth is a brittle, crystalline **metal** that is white with a pinkish tint. It is the heaviest and only nontoxic member of the **heavy metals**. Its name is derived from the German *Wismut* ("white metal"), which was Latinized to *bisemutum* by G. Bauer in 1530. In early years it was confused with tin and lead. Bismuth has only one naturally occurring **isotope**, ^{209}Bi (the heaviest stable isotope of any element).

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

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

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

Peru, Japan, Mexico, and Canada are the main producers of bismuth. It can be found in several ores: bismuthinite (Bi_2S_3), bismite (Bi_2O_3), and bismutite $(BiO_2)CO_3$. It is also obtained as a by-product of the refining of silver and gold ores in the United States. Bismuth has an abundance in Earth's crust of 0.008 parts per million.

Bismuth commonly forms cations of +3 charge. It forms the basic oxide Bi_2O_3 and salts of oxoacids such as $Bi_2(SO_4)_3$ and $Bi(NO_3)_3$. Reaction of the metal with halides such as fluorine and chlorine results in a salt with the formula of BiX_3. Because of the size of the metal atom, the linkages are more ionic than those found for other group members.

Bismuth is the most **diamagnetic** of all metals and has low thermal conductivity. Since bismuth expands upon solidification, it is used to make castings for objects subjected to high temperatures. It is used as a replacement for lead in solders, shot for hunting, fishing sinkers, ceramic glazes, and brasses for plumbing applications. It is also used as a carrier for ^{235}U (an isotope of uranium) fuel in atomic reactors. Ionic compounds of bismuth are used in cosmetics and medicine.

diamagnetic: property of a substance that causes it to be repelled by a magnetic field

Catherine H. Banks

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Black, Joseph

SCOTTISH CHEMIST AND PHYSICIST
1728–1799

Joseph Black was trained as a medical doctor. One of his early scientific undertakings was investigating means of treating "the stone" (kidney stones and gallstones). The investigation prompted him to make a study of how to dissolve stones found in nature. Black found that certain stones, such as limestone, dissolved in mild acids, giving off large volumes of a gas. He called this gas "fixed air," as it had been "fixed" in a small volume of solid stone.

Following the practice of the **pneumatic chemists** (chemists who were studying the properties of gases or "airs"), he trapped and characterized this new gas. "Fixed air" was found to be mildly acidic. It would later be called carbon dioxide, and stones that generated this gas would be defined as carbonates. Black also discovered that the chemical nature of the gas that had been produced in these experiments was determined by the stone it came from, not by the acid used.

pneumatic chemist: early chemist who studied primarily the properties of gases

Black was the first to distinguish between the temperature of an object and the heat contained in that object. He characterized "specific heat" as the amount of heat required to increase the temperature of a sample by a given amount. He recognized that it is dependent on the identity of and the amount of the material in the sample. If the sample being heated is at its melting or boiling temperature prior to the application of heat, it will absorb heat as it is going through a **phase** change (from solid to liquid or liquid to gas), but the temperature of the sample does not increase. The amount of heat absorbed during such a transition is also dependent on the amount of material in the sample and is characteristic of the type of material in the sample. Black termed this heat "latent heat" because it is "latent" in the sample and does not increase the temperature of the sample.

phase: homogeneous state of matter

Although trained as a medical doctor, Joseph Black spent most of his professional career as an instructor in chemistry at the University of Edinburgh. His lecture notes were edited by one of his students and published as a textbook in chemistry in 1803, four years after his death.

David A. Bassett

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Bleaches

When chlorine gas is bubbled through a cylinder of tomato juice, the chlorine/tomato juice mixture turns almost completely white within five minutes. This spectacular change is a result of the chemical action of chlorine, acting as an oxidizing bleaching agent, on the pigments in tomato juice. When old newspaper clippings, discolored through aging and exposure to light, are treated with 1 percent aqueous sodium borohydride solution, the paper is dramatically whitened within twenty minutes. In this instance, the paper has been restored to its original white color by the action of sodium borohydride acting as a reducing bleaching agent.

A bleaching agent is a substance that can whiten or decolorize other substances. Colored substances generally contain groups of atoms, called **chromophores**, that can absorb visible light having specific, characteristic wavelengths, and reflect or transmit the part of light that is not absorbed. For example, if a chromophore absorbs blue light, it will reflect light of the complementary color, and the chromophore-containing substance will appear yellow. Bleaching agents essentially destroy chromophores (thereby removing the color), via the **oxidation** or reduction of these absorbing groups. Thus, bleaches can be classified as either oxidizing agents or **reducing agents**.

chromophore: part of the molecule that yields characteristic colors

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

reducing agent: substance that causes reduction, a process during which electrons are lost (or hydrogen atoms gained)

Some of the use of bleaching agents are:

- The bleaching of textiles and fabrics
- The bleaching of wood pulp
- The removal of stains
- Commercial and household laundering and cleaning
- As ingredients in scouring cleansers and dishwashing products
- The bleaching of hair

Oxidizing Bleaches

A large number of oxidizing bleaches were reviewed by Jules A. Szilard in *Bleaching Agents and Techniques* (1973). The oxidizing bleaches (and bleaching agents) in common use today are: chlorine, chlorine dioxide, alkaline hypochlorites, hydrogen peroxide, peroxygen compounds, and sunlight and artificial light.

Chlorine (Cl_2). The discovery of chlorine by the Swedish chemist Carl Wilhelm Scheele in 1774 marked the beginning of the modern era of bleaching. According to Sidney M. Edelstein in a 1948 journal article titled "The Role of Chemistry in the Development of Dyeing and Bleaching," French chemist Claude-Louis Berthollet was the first to use chlorine to bleach cotton and linen fabrics.

Chlorine has been used to bleach wood pulp. Many pulp mills employing the Kraft pulping process prepare sodium hydroxide (needed to digest wood chips) on-site via the electrolysis of **brine**, a concentrated **aqueous solution** of sodium chloride.

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

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

$$2NaCl + 2H_2O \rightarrow 2NaOH + H_2 + Cl_2 \qquad (1)$$

Chlorine is a side product. Subsequent chlorine bleaching of the brown pulp gives a product that can be used for the manufacture of writing and printing paper. Unfortunately, organic compounds in the pulp are both oxidized and chlorinated, yielding small quantities of organochlorine compounds, in-

BLEACHING AGENTS AND USES

Bleaching Agent	Commercial Use in Bleaching
Chlorine	Bleaching pulp and paper; making hypochlorites
Chlorine dioxide	Bleaching kraft paper and flour
Sodium hypochlorite	Household laundering and sanitizing
Calcium hypochlorite	Solid bleach used in sanitizing
Sodium dichloroisocyanurate	Sanitizing and dishwashing agents
Hydrogen peroxide	Bleaching textiles, fur, pulp and paper, and hair
Sodium perborate	Milder bleach for laundering; dry cleaning; denture cleaning; tooth powder; replacement for phosphates in detergents
Light	Bleaching paper artifacts
Sulfur dioxide	Preserving grapes, wine, and apples; removal of color during refinement of sugar
Sodium sulfite; sodium bisulfite	Anti-chlor (a reducing agent for removing oxidizing bleaches)
Sodium dithionite	Bleaching textiles, pulp and paper; removing rust stains
Sodium borohydride	Bleaching pulp and paper

Table 1. Bleaching agents and their commercial uses.

cluding dioxins. In fact, the most abundant dioxin produced by the pulp and bleaching process, 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (2,3,7,8-TCDD), has been found to be both a carcinogen and a deadly **toxin**. Thus, chlorine as a bleaching agent is being replaced by the safer bleaching agents chlorine dioxide and hydrogen peroxide. In fact, the trend in the pulp and paper industries is toward totally chlorine free (TCF) bleaching. Chlorine is now used in the bleaching industry mainly to prepare hypochlorite solutions and dry bleaches such as calcium hypochlorite.

toxin: poisonous substance produced during bacterial growth

Chlorine Dioxide (ClO_2). Chlorine dioxide has been used as a bleaching agent both in its gaseous **phase** and in aqueous solution. Because of its explosive nature, chlorine dioxide in the gaseous phase is often diluted with nitrogen or carbon dioxide. If stored or shipped, chlorine dioxide is passed through cold water and kept under refrigeration.

phase: homogeneous state of matter

Chlorine dioxide is prepared industrially via the reduction of sodium chlorate by sulfur dioxide in aqueous solution.

$$2NaClO_3 + SO_2 + H_2SO_4 \rightarrow 2ClO_2 + 2NaHSO_4 \qquad (2)$$

A relatively safe method for the preparation of ClO_2 involves the reaction between sodium chlorite ($NaClO_2$) and **formaldehyde** (H_2CO).

$$H_2CO + H^+ + ClO_2^- \rightarrow HOCl + HCOOH \qquad (3)$$

formaldehyde: name given to the simplest aldehyde HC(O)H, incorporating the −C(O)H functional group

As reaction 3 proceeds, the pH of the solution drops (due to the production of formic acid [HCOOH]). The increased acidity of the solution promotes the formation of ClO_2, shown in equation 4.

$$HCOOH + HOCl + 2ClO_2^- \rightarrow 2ClO_2 + Cl^- + H_2O + HCOO^- \qquad (4)$$

In acidic solution, chlorine dioxide behaves as an oxidizing agent. The complete reduction of ClO_2 is shown in equation 5.

$$ClO_2 + 4H^+ + 5\ e^- \rightarrow Cl^- + 2H_2O \qquad (5)$$

The individual steps of this overall reduction reaction produce $HClO_2$, HOCl, and Cl_2, which all behave as oxidizing agents. An acidic medium is required, as ClO_2 disproportionates in alkaline solution, as shown in equation 6.

$$2ClO_2 + 2OH^- \rightarrow ClO_3^- + ClO_2^- + H_2O \qquad (6)$$

Chlorine dioxide is mainly used for pulp bleaching.

Hypochlorites (OCl^-). Hypochlorite bleach solutions are made from NaOCl and, to a lesser extent, $Ca(OCl)_2$. Hypochlorites are used in laundering, as disinfectants, in the bleaching of pulp and textiles, and in the removal of ink from recycled paper. Commercial bleaching solutions are obtained by passing chlorine gas through cold, dilute, aqueous sodium hydroxide, as shown in equation 7.

$$Cl_2 + 2OH^- \rightarrow OCl^- + Cl^- + H_2O \qquad (7)$$

Alternatively, the hypochlorite ion can be generated by the hydrolysis of organic nitrogen-chlorine compounds. Some of the more important nitrogen-chlorine compounds used in this way are the chlorinated isocyanurates. These find use in cleansing and dishwasher products.

To be an effective bleach, the hypochlorite solution should be kept alkaline ($pH > 9.0$), in order to suppress the hydrolysis of OCl^- (see equation 8) and prevent the formation of unstable HOCl.

$$OCl^- + H_2O \rightarrow HOCl + OH^- \qquad (8)$$

In acidic solutions, HOCl forms and decomposes.

$$3HOCl \rightarrow HClO_3 + 2HCl \qquad (9)$$

HOCl will also react with HCl, one of the decomposition products.

$$HOCl + HCl \rightarrow H_2O + Cl_2 \qquad (10)$$

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

Hypochlorite bleaching solutions must not contain **heavy metal** cations, as these cations (like light or heat) promote the decomposition of HOCl, as shown in equation 11.

$$2HOCl \rightarrow 2HCl + O_2 \qquad (11)$$

The active ingredients in hypochlorite bleaches vary with pH. At $pH < 2$, Cl_2 is the main component in solution; at pH 4 to 6, HOCl is the dominant species; at $pH > 9$, OCl^- is the only component present. It is the hypochlorite ion in basic solution that is the active ingredient in household bleach, which is typically about 5 to 6 percent NaOCl. The OCl^- ion oxidizes chromophores in colored materials, and is itself reduced to chloride and hydroxide ions.

$$OCl^- + H_2O + 2\ e^- \rightarrow Cl^- + 2OH^- \qquad (12)$$

The whitening process effected by commercial hypochlorite bleach is often enhanced by the use of optical brighteners, compounds that absorb incident ultraviolet light and emit visible light, making the fabric appear brighter and whiter.

Hydrogen Peroxide (H_2O_2). Hydrogen peroxide can be prepared by the reaction of barium peroxide and sulfuric acid (see equation 13). As barium sulfate precipitates out, hydrogen peroxide is easily separated.

$$BaO_2 + H_2SO_4 \rightarrow BaSO_4 + H_2O_2 \qquad (13)$$

Hydrogen peroxide, as a bleaching agent used in the pulp and paper industry, has the advantage that it is nonpolluting. Because of the instability of pure hydrogen peroxide, aqueous solutions are employed in bleaching. At room temperature, hydrogen peroxide very slowly decomposes to water and oxygen.

$$2H_2O_2 \rightarrow H_2O + O_2 \qquad (14)$$

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

However, the presence of **transition metal** cations (particularly Fe^{3+}, Mn^{2+}, and Cu^{2+}) and other catalysts dramatically accelerates this reaction. As a result, aqueous hydrogen peroxide must be stabilized with complexing agents that sequester transition metal cations.

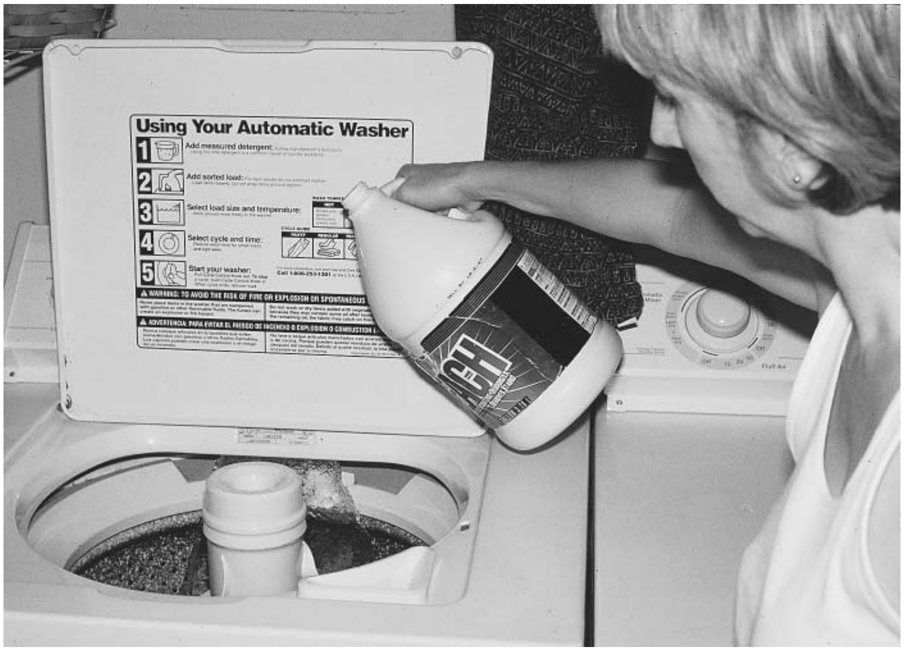
anion: negatively charged chemical unit, like Cl^-, CO_{32}^-, or NO_3^-

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

The active bleaching species in hydrogen peroxide is the perhydroxyl **anion**, OOH^-, formed through the **ionization** of H_2O_2.

$$H_2O_2 + H_2O \rightarrow H_3O^+ + OOH^- \qquad (15)$$

The acid ionization constant of hydrogen peroxide is very low ($K_a = 2 \times 10^{-12}$) with the result that solutions of H_2O_2 must be made alkaline in or-



This woman is using bleach to launder clothing. Not only can bleach remove stains, but it can act as an agent to remove color.

der to raise the concentration of OOH^-. In the absence of an alkaline medium, hydrogen peroxide is no longer effective as a bleaching agent. For example, the bleaching stage of hair dyeing often employs hydrogen peroxide (5–6%), but also ammonia to provide an alkaline medium.

At the same time the pH must not rise above 11, as at this point the decomposition of OOH^- begins to occur.

$$2OOH^- \rightarrow O_2 + 2OH^- \qquad (16)$$

Peroxygen Compounds. A number of solid peroxygen compounds that release hydrogen peroxide when dissolved in water exist. These include sodium perborate ($NaBO_3 \cdot 4H_2O$ or $NaBO_2 \cdot H_2O_2 \cdot 3H_2O$) and sodium carbonate peroxyhydrate ($2Na_2CO_3 \cdot 3H_2O_2$). The structure of sodium perborate contains the peroxoanion $B_2(O_2)_2(OH)_4^{2-}$, which contains two O–O linkages that join two tetrahedral $BO_2(OH)^{2-}$ groups. These peroxygen compounds are used in detergents, denture cleaners, and tooth powders.

Bleaching with Light. Bleaching that involves either natural sunlight or artificial light has been used to remove stains from paper artifacts and to treat textiles. The material to be bleached is first immersed in an alkaline solution of either calcium or magnesium bicarbonate, and then protected from **ultraviolet radiation** by covering it with Plexiglas, Lexan, or Mylar. Exposure to light is then allowed to take place for two to four hours, for natural sunlight, and two to twelve hours, for artificial light.

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

Reducing Bleaches

Reducing agents used in bleaching include sulfites, bisulfites, dithionites, and sodium borohydride, all of which are used in pulp and textile bleaching.

Sulfites (SO_3^{2-}) and Bisulfites (HSO_3^-). The oxidation state of sulfur in both SO_3^{2-} and HSO_3^- is +4, and oxidation to +6 occurs readily, with the formation of SO_4^{2-} and HSO_4^-, respectively, making sulfites and bisulfites good reducing agents.

Dithionites ($S_2O_4^{2-}$). Both sodium and zinc dithionite have found use in the bleaching of mechanical pulps and textiles. The preparation of the dithionite ion is accomplished via the reduction of the bisulfite ion and sulfur dioxide with Zn dust.

$$2HSO_3^- + SO_2 + Zn \rightarrow Zn^{2+} + S_2O_4^{2-} + SO_3^{2-} + H_2O \quad (17)$$

The dithionite ion, $S_2O_4^{2-}$, which has sulfur in the +3 oxidation state, behaves as a strong reducing agent in alkaline solution.

$$S_2O_4^{2-} + 4OH^- \rightarrow 2SO_3^{2-} + 2H_2O + 2\ e^- \quad (18)$$

As the pH is lowered, the reducing power of the dithionite ion drops off, as predicted by LeChatelier's principle.

Dithionites are useful in removing rust stains, and neutral citrate solutions of $Na_2S_2O_4$ were used to remove iron corrosion products from objects recovered from the *Titanic.*

Sodium Borohydride ($NaBH_4$). Sodium borohydride has been used mainly in the industrial bleaching of mechanical pulps. The BH_4^- ion is a strong reducing agent in alkaline solution.

$$BH_4^- + 10OH^- \rightarrow BO_3^{3-} + 8\ e^- + 7H_2O \quad (19)$$

One problem with using sodium borohydride is that the BH_4^- ion slowly decomposes in aqueous solution.

$$BH_4^- + 4H_2O \rightarrow B(OH)_4^- + 4H_2 \quad (20)$$

As an alternative method, BH_4^- salts may be dissolved in either CH_3OH or the less toxic C_2H_5OH. The decomposition of the BH_4^- ion in alcohols occurs at a much slower rate:

$$BH_4^- + 4ROH \rightarrow B(OR)_4^- + 4H_2 \qquad (R = CH_3, C_2H_5) \quad (21)$$

Conclusion

A bleaching agent can whiten or decolorize a substance by reacting with the chromophores that are responsible for the color of the substance. Depending on the nature of the chromophores, the bleaching agent will either be an oxidizing or reducing agent. That is, the chromophore is either oxidized or reduced to produce a colorless or whitened substance. Bleaching agents and their commercial uses are summarized in Table 1. SEE ALSO BERTHOLLET, CLAUDE-LOUIS; CHLORINE; DETERGENTS; SCHEELE, CARL.

Henry A. Carter

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Blood ***See Hemoglobin.***

Bohr, Niels

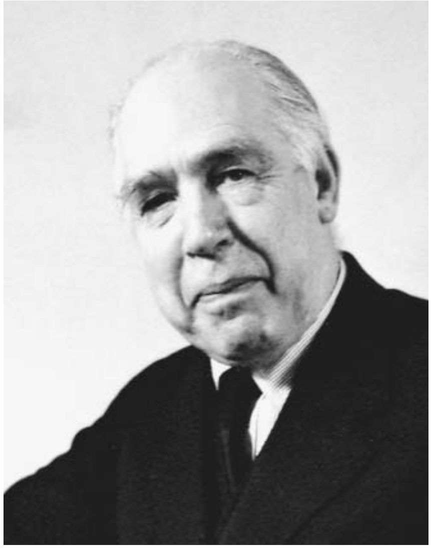
DANISH PHYSICIST
1885–1962

nuclear: having to do with the nucleus of an atom

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

Niels Bohr was one of the founders of modern atomic and **nuclear** physics. He was born into a family of intellectual and academic distinction. His father, Christian Bohr (1855–1911), was a professor of physiology; his brother, Harald Bohr (1887–1951), was a professor of mathematics; and his son, Aage Bohr (b. 1922), a professor of physics—all of them at the University of Copenhagen.

Niels Bohr studied at the University of Copenhagen and earned a master of science degree in 1909 and a doctorate degree in 1911 (at the age of twenty-six). He then went to England and worked with Joseph John Thomson at Cambridge University and with Ernest Rutherford at Victoria University in Manchester. In 1914 Bohr returned to the University of Copenhagen, where, at the age of twenty-nine, he became an assistant professor of physics (he became a full professor in 1916 and held that post until 1956). From 1920 onward he was the director of the university's Institute for **Theoretical Physics** (renamed the Niels Bohr Institute in 1965). The institute became a focal center for theoretical physics for a generation.



Danish physicist Niels Henrik David Bohr, recipient of the 1922 Nobel Prize in physics, "for his services in the investigation of the structure of atoms and of the radiation emanating from them."

In 1913 Bohr (while still in England) published three papers on the quantum theory of atoms. He explained that atoms exist in "stationary" states, and that when an atom changes from one state to another, there has been an emission (or absorption) of electromagnetic radiation of frequency ν, determined by the energy difference between the two states.

$$\Delta E = E_2 - E_1 = h\nu.$$

The constant h is Planck's constant. With this theory Bohr combined the atomic model of Rutherford with existing quantum theory, and he made it clear that classical physics was not sufficient to describe atoms or their behaviors. At first the Bohr theory was a theory that explained the behavior of hydrogen atoms. In the years to come he extended the theory to encompass all elements and to provide an explanation of the Periodic Table. The Bohr radius (52.9×10^{-12} m) and the Bohr magneton (9.27×10^{-24} J/T) are today used as units of measure. In 1922 Bohr received the Nobel Prize in physics.

Bohr deduced the correspondence principle: A quantum description of atoms must tend to the classical description for larger dimensions. He also deduced the complementarity principle: There are interactions between objects and the instruments used to observe them. Using the complementarity principle he concluded that there is always a limit to the ability of scientists to observe (and to know) atoms. With this concept he acquired an influence beyond the world of physics.

fission: process of splitting of a heavy atom into smaller pieces

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

In the 1930s Bohr turned to nuclear physics. In 1936 he described an atomic nucleus as resembling a liquid drop existing in different states. In 1940 he and John Archibald Wheeler devised a theory of the **fission** of atoms, in it explaining the phenomenon of the accompanying release of atomic energy. In that same year Denmark was occupied by German military forces, and in 1943 Bohr fled to the United States via Sweden and England. In the United States he became a member of the **Manhattan Project**. After the war he returned to Denmark, where he continued to conduct research in atomic and nuclear physics.

In 1950 Bohr wrote an open letter to the United Nations warning of the horrors of nuclear war. In 1955 he organized the first Atoms for Peace Conference. Niels Bohr was one of the greatest scientists of the twentieth century. SEE ALSO RUTHERFORD, ERNEST; THOMSON, JOSEPH JOHN.

Ole Bostrup

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Boltzmann, Ludwig

AUSTRIAN PHYSICIST
1844–1906

kinetic theory: theory of molecular motion

Ludwig Edward Boltzmann is one of the foremost theoretical physicists of the latter nineteenth century. A vigorous advocate for the existence of atoms, he made monumental contributions to the **kinetic theory** of gases and established the statistical nature of the second law of thermodynamics.

Boltzmann was born in Vienna, Austria, and graduated from high school in Linz. He entered the University of Vienna in 1863, and he received his doctorate in physics three years later. Then, for two years, he served as assistant professor at the university, where he was strongly influenced by the atomistic thinking of physicists Josef Loschmidt and Josef Stefan.

In 1869 Boltzmann became professor of mathematical physics at the University of Graz, the first of his many academic appointments. After leaving Graz in 1873, he held chairs in mathematics at Vienna (1873–1876), experimental physics at Graz (1876–1890), and **theoretical physics** at Munich (1890–1893), Vienna (1893–1900), Leipzig (1900–1902), and finally Vienna again for the remaining four years of his life. According to many of his students, Boltzmann was an outstanding teacher, and his lectures were often filled to overflowing. He displayed a congenial attitude toward students and their learning, something rather rare among Austrian and German professors at that time.

Austrian physicist Ludwig Boltzmann, who established the statistical nature of the second law of thermodynamics.

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

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

Boltzmann's first significant contribution to physics was the generalization of James Clerk Maxwell's distribution of velocities and energies for a sample of gaseous atoms. Although Maxwell had deduced this distribution, he provided no physical basis for it. Boltzmann showed that as atoms move toward **equilibrium** they assume the Maxwell distribution—later known as the Maxwell-Boltzmann distribution—and further that this is the only statistically possible distribution for a system at equilibrium.

Boltzmann connected his ideas with those of Rudolf Clausius, who had introduced the concept of entropy in 1865. Somehow related to heat, entropy was known to increase during irreversible processes, but its exact nature was unknown. From the distribution of gas atoms, Boltzmann described a quantity—later symbolized by the letter H—which is a minimum when atoms assume a Maxwell-Boltzmann distribution. He recognized his H function as the negative of entropy, which is a maximum when the atoms reach thermal equilibrium. Thus Boltzmann offered a kinetic explanation for entropy and, more generally, a connection between the behavior of atoms and thermodynamics.

One of the serious problems with Boltzmann's statistical treatment arose from the reversibility of the laws of mechanics, which holds true for a particle moving in one direction just as they do for a particle moving in the opposite direction. How then could a given set of atomic motions cause H to tend toward a minimum (or entropy toward a maximum), rather than away from it? This was a vexing question for Boltzmann and a serious criticism of kinetic theory.

In response, Boltzmann considered the number of different ways that a sample of gaseous atoms could achieve a particular distribution. The more ways the atoms can arrange themselves to achieve some distribution, the more likely it becomes for that distribution to occur. This connection between entropy (S) and the number of ways (W) that a given distribution can occur is embodied in the equation $S = k \ln W$ (k is now known as Boltzmann's constant, and ln is the natural logarithm). This famous relationship, which is engraved on Boltzmann's gravestone in Vienna, indicates that maximum entropy is associated with the distribution that has the most ways of occurring, that is, with the Maxwell-Boltzmann distribution. Although it is possible for a system of atoms to move away from a Maxwell-Boltzmann distribution, it is not probable, since it is statistically unlikely for the system to move from a distribution with more ways of achieving it to one with fewer ways. Much of Boltzmann's work in this area was formalized somewhat differently under the name of statistical mechanics by Josiah Willard Gibbs, an American physicist who was well known and well respected in Europe, but not in his own country.

Boltzmann's achievements in theoretical physics are all the more remarkable in view of the considerable opposition to his ideas and in view of his own declining health. He had increasingly severe bouts of mental depression, and he tried to commit suicide several times during his life. In 1906 he succeeded in hanging himself while vacationing with his wife and family at Duino, near Trieste, on the Adriatic Sea. SEE ALSO GIBBS, JOSIAH WILLARD; MAXWELL, JAMES CLERK.

Richard E. Rice

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Bonding

In the everyday world around us, we observe three very different types of materials: gases, liquids, and solids. Closer examination of the physical properties of **homogeneous** crystalline solids shows that they can be subdivided into four distinct categories according to their physical properties and the different forces holding them together. For each category, we must develop a bonding picture, based on electrons, that will lead to an understanding of the physical properties exhibited. We can classify the solids according to the distribution of the **valence** electrons of the atoms (as shown in Figure 1), which explains their physical properties.

homogeneous: uniform throughout

valence: combining capacity

Types of Solids

Metallic. A **metal** is a substance that can conduct electricity both as a solid and when it is molten. The range of melting points for metals is very large, from −39°C for mercury to 1,083°C for copper and 3,200°C for tungsten. The outermost valence electrons of the atoms belong to the crystal as a whole, **delocalized** as a "sea" in which they are freely mobile to flow from

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

delocalized: of a type of electron that can be shared by more than one orbital or atom

atom to atom. The positive nuclei of the atoms are embedded in the sea as a close-packed three-dimensional array.

Ionic. Ionic materials are those that are brittle and that conduct electricity when molten but not as solids. Melting points range upwards from about 500°C. Examples are CaO (quicklime), MgF_2, and NaCl (common table salt). The electrons are constrained about each atom, some atoms with excess positive charge (cations) and some with excess negative charge (**anions**). The ions are packed closely together, held by coulomb (electrostatic) forces of **attraction**.

Covalent network. A solid that is extremely hard, that has a very high **melting point**, and that will not conduct electricity either as a solid or when molten is held together by a continuous three-dimensional network of **covalent bonds**. Examples include diamond, quartz (SiO2), and silicon carbide (SiC). The electrons are constrained in pairs to a region on a line between the centers of pairs of atoms.

Van der Waals molecular. A material that has a very low melting point and that will not conduct electricity either as a solid or when molten consists of molecules that are close-packed, bump-in-hollow and that are attracted to each other by weak van der Waals attractions. Examples include carbon dioxide (CO_2, dry ice), iodine (I_2), and naphthalene (mothballs). The electrons are constrained to the well-defined groups of atoms that constitute the molecules. The atoms within the molecules are linked together by strong covalent bonds. The weak attractions between the molecules, termed London forces, arise from the charge asymmetry in the molecules that result from the polarizability of their electron clouds.

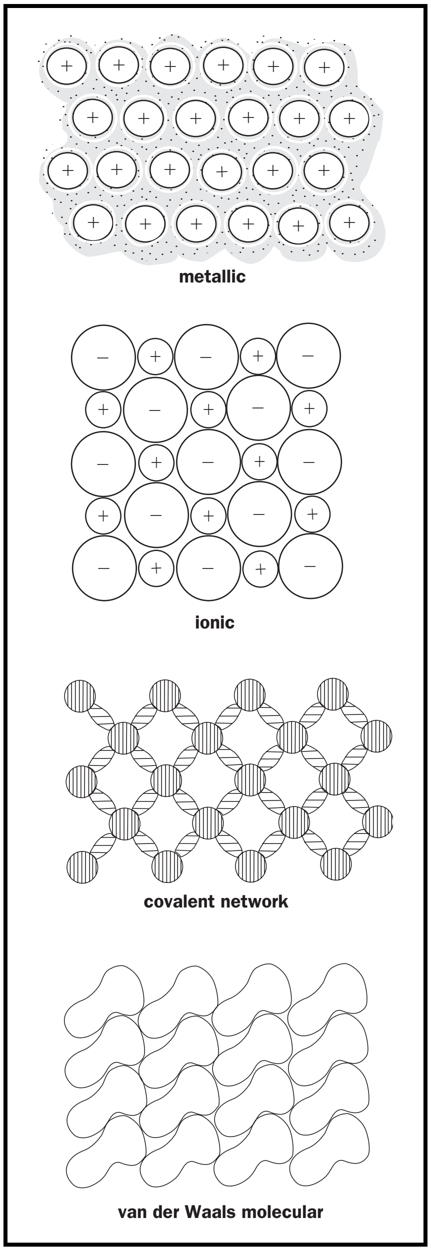


Figure 1. Schematic representation of the packing of the atoms and the electron distribution in the four types of solids.

The Tetrahedron of Bonding Types

These four extreme types of bonding can be represented on the four apexes of a tetrahedron. (See Figure 2.)

The various intermediate types of bonding lie along the edges. Choosing examples that exemplify the extreme types of bonding is straightforward. It is far more difficult to identify appropriate solids to illustrate the six intermediate cases (those that lie along the edges of the tetrahedron), yet it is these very materials that are the most interesting and that often have important applications. The criteria for selecting them must include

- Melting point;
- Conductance as a solid;
- Conductance when molten;
- Pattern and number of close contacts in the solid; and
- Atom-atom distances in the solid

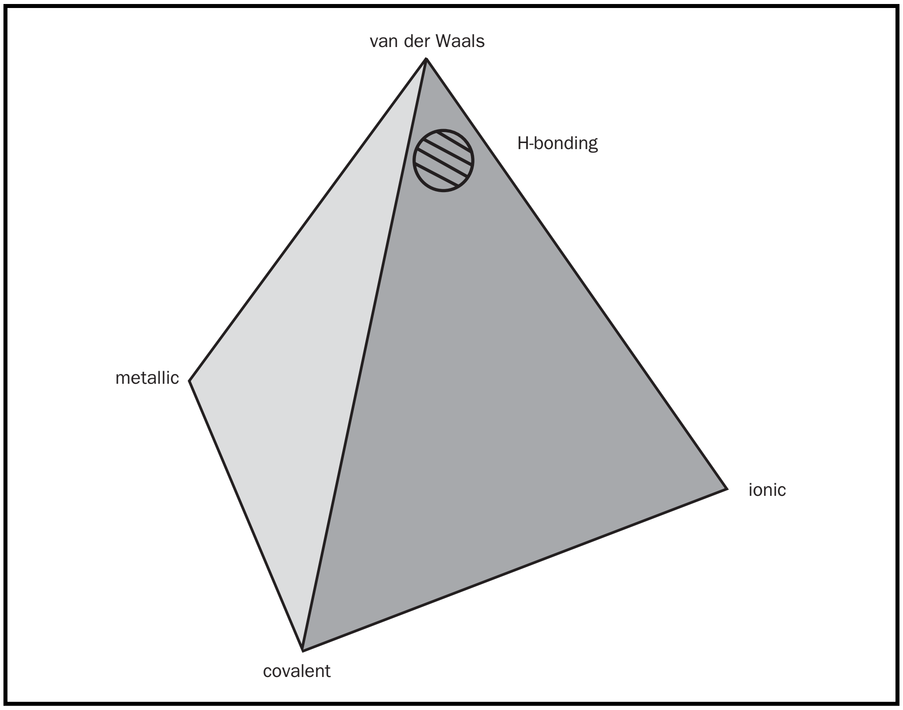
because these are the properties that characterize the four extreme types of bonding.

Metallic Bonding

Metals are unique in that they can conduct electric current in the solid state. (Examples include aluminum high **voltage** transmission cables and copper

voltage: potential difference expressed in volts

Figure 2. The tetrahedron of bonding types. Typical examples are: metallic-copper; ionic-NaCL; covalent network-diamond; van der Waals, molecular-iodine. Hydrogen bonding would be represented by the cross-hatched area near to van der Waals types of bonding.



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

wire in domestic wiring.) Also, metals are **ductile** and malleable; they can be hammered into sheets, such as the pressed steel used as body parts for a car. The layers of atoms can slide past each other on a cushion of electrons, yet the solid remains whole. (See Figure 1.)

In many metals, each atom is in contact with twelve others: six in a plane, three above, and three below. These are termed close-packed hexagonal (e.g., magnesium), or face-centered cubic (e.g., copper). In other metals (e.g., iron), each atom is in contact with eight others at the corners of a cube; such structures are called body-centered cubic.

To a first approximation, we expect that the melting point of the metal should be related to the number of valence electrons that each atom contributes to the "sea." Two series of metals, as outlined in Table 1, illustrate the effect.

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

The simple model fits observation remarkably well for pure metals. However, this model begins to fail for **alloys** (solutions of one metal in another), such as brass and bronze, where for certain stoichiometries the material has anomalous physical properties and behaves almost as a compound (e.g., CuZn and Cu5Sn, termed Hume-Rothery electron phases).

MELTING POINTS OF METALS

Group in the Periodic Table	1	2	3	4
Metal	K	Ca	Sc	Ti
Melting point (°C)	64	850	1,539	1,875
Metal	Rb	Sr	Y	Zr
Melting point (°C)	39	770	1,509	1,852

Table 1. Melting points of metals.

PROPERTIES OF IONIC COMPOUNDS

Compound	$q^+ \times q^-$	Lattice Energy (kJ/mole)	Melting Point (°C)	Solubility in Water
NaCl	$1 \times 1 = 1$	770	808	Soluble
CaF_2	$2 \times 1 = 2$	2,610	1,418	Insoluble
MgO	$2 \times 2 = 4$	3,906	3,070	Insoluble

Table 2. Properties of ionic compounds.

Ionic Bonding

When two elements of very different groups in the Periodic Table react (e.g., the metals Na and Mg from Groups 1 and 2 on the left side with the nonmetals O_2 and Cl2 from Groups 6 and 7 on the right side), the product is a solid (usually colorless) that has a high melting point. The product is an insulator but will conduct electricity in the molten state. The solid is built of alternating positively charged cations and negatively charged anions, packed tightly together, the exact pattern depending on the charges on the ions, q^+ and q^-, and on their relative sizes—the radius ratio r_+/r_-. In general, the metal atom loses electrons to leave a cation with a closed shell—an octet, at the cost of the **ionization** energy (IE): $Na° - e^- \rightarrow Na^+$. A **halogen** atom will acquire an electron to form an anion with a closed shell, releasing energy, the electron affinity (EA): $F + e^- \rightarrow F^-$.

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

halogen: element in the periodic family numbered VIIA (or 17 in the modern nomenclature) that includes fluorine, chlorine, bromine, iodine, and astatine

The attractive forces within the crystalline ionic structure are of the form $M\,(q^+ \times q^-)/(r_+ + r_-)^2$, where the value of M, the Madelung constant, depends on the pattern of packing of the ions. We can expect that the product $(q^+ \times q^-)$ should give an indication of the cohesive energy of the solid. (See Table 2.)

A large value of the **lattice** energy indicates very strong bonding in the solid, hence a high melting point, and insolubility in water. The face-centered cubic structure adopted by the ionic compounds NaCl and MgO is shown in Figure 3. The small spheres represent the cations, and the large spheres represent the anions.

lattice: systematic geometrical arrangement of atomic-sized units that constitute the structure of a solid

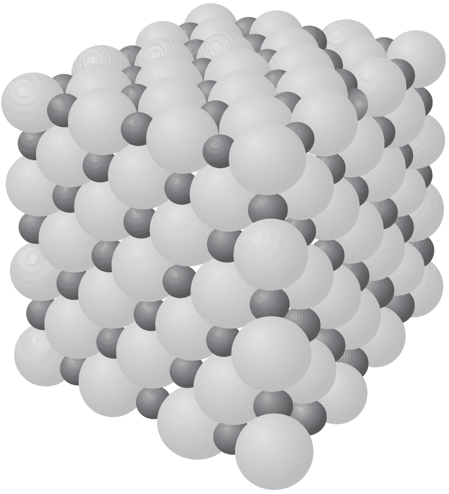
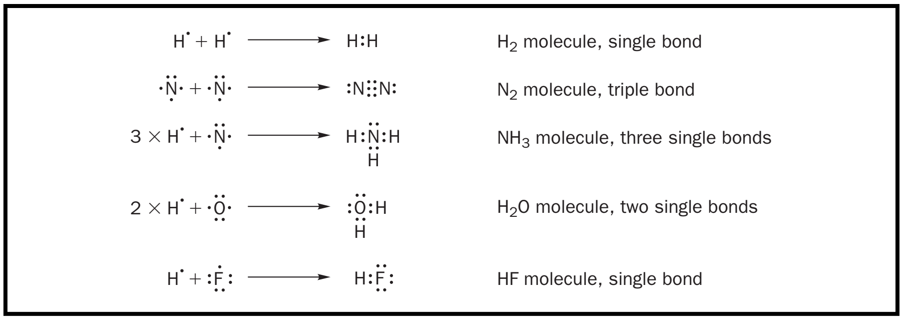


Figure 3. Face-centered cubic structure of NaCl and MgO crystals.

Figure 4. Electron pair bonding in simple molecules. Each H atom shares two electrons, each of the other atoms has four pairs.



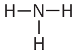
Covalent Bonding

This type of bonding is found between pairs of similar atoms, especially among those in the upper right hand corner of the periodic table. For example, C—C in hydrocarbons, S—O in sulfur dioxide, C—F in Freons. The bonds can give rise to three-dimensional structures like diamond, and are found in simple molecules like H_2S. These bonds are strong, and result in molecules with fixed geometry, such as methane, and give rise to optical activity in molecules such as lactic acid where the C atom is rigidly bonded to four different groups.

Pairs of electrons. Covalent bonding occurs between two atoms as a result of the sharing of a pair of electrons between the atoms. An example is provided in Figure 4.

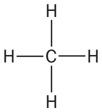
Octets and Lewis Structures When bonded, atoms of the elements C, N, O, and F always tend to be associated with eight electrons in the valence shell—the "octet." The simultaneous attaining of a pair of electrons per covalent bond and an octet around the heavy atom is a powerful bookkeeping method of accounting for the bonding in molecules of the lighter main group elements in the periodic table. The diagrams are termed Lewis structures. The three-dimensional network structures are built around atoms with four bonds in a tetrahedron. For example, in diamond each carbon atom shares electrons with four neighbors to give four covalent bonds in a tetrahedral array. (See Figure 5.)

The diamond crystal can thus be imagined as a huge carbon molecule (C_x). If the pairs of electrons in the diagrams are replaced by lines to represent the covalent bonds, ammonia becomes



$$\begin{array}{c} H-N-H \\ | \\ H \end{array}$$

and methane becomes



$$\begin{array}{c} H \\ | \\ H-C-H \\ | \\ H \end{array}$$

Each straight line represents a localized two-center two-electron bond. In the ammonia molecule, one pair of electrons on the nitrogen atom is not involved in directly bonding to the H atoms; this is termed a lone pair. Unfortunately these Lewis diagrams can say nothing about the shape of the

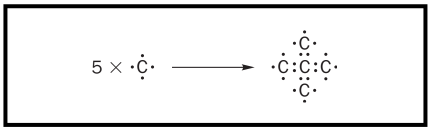


Figure 5. Octet of electrons about the carbon atom in diamond.

molecule. This comes much later by the Sidgwick-Powell/Gillespie-VSEPR approach to molecular geometry.

If we apply the Lewis formalism to the diatomic molecules of nitrogen, oxygen, and fluorine, we get

$$:N{\vdots}{\vdots}N: \qquad \overset{..}{\underset{..}{O}}::\overset{..}{\underset{..}{O}} \qquad :\overset{..}{\underset{..}{F}}:\overset{..}{\underset{..}{F}}:$$

N≡N, a triple bond O=O, a double bond F—F, a single bond

The three molecules obey the octet rule, and in each case all of the electrons are paired. The experimental facts show that for oxygen this bonding picture is wrong: Oxygen is paramagnetic; that is, the molecule has two unpaired electrons. This simplistic picture has failed, and a new approach to covalent bonding is required.

There are two other approaches to understanding covalent bonding: the molecular orbital (MO) theory and the valence bond (VB) theory. The VB approach is useful when considering molecular geometry. The MO approach is important when considering electronic spectra and other energy properties of the molecule. These topics are discussed separately.

Hybrid atomic orbitals and shapes of molecules. The valence electrons of the light elements lithium to fluorine are distributed in **atomic orbitals** 2s, $2p_x$, $2p_y$, and $2p_z$, whose shapes are given in Figure 6.

atomic orbital: mathematical description of the probability of finding an electron around an atom

If they are close in energy, the s and p orbitals of an atom can interact to give combinations of different geometry, called hybrid atomic orbitals. This is nicely seen in the simple hydrocarbons, because the energy gap between the 2s and 2p orbitals in the carbon atom is relatively small, about 4 electron volts compared to 16 electron volts in the oxygen atom. The combination of one s plus three p orbitals gives four sp^3 hybrid orbitals oriented in a tetrahedron, with an interorbital angle of $109\frac{1}{2}°$. The combination of one s plus two p orbitals gives three sp^2 hybrid orbitals arranged in a trigonal plane, with an interorbital angle of 120°. The combination one s plus one p orbital gives two collinear sp hybrid orbitals. (See Figure 7.)

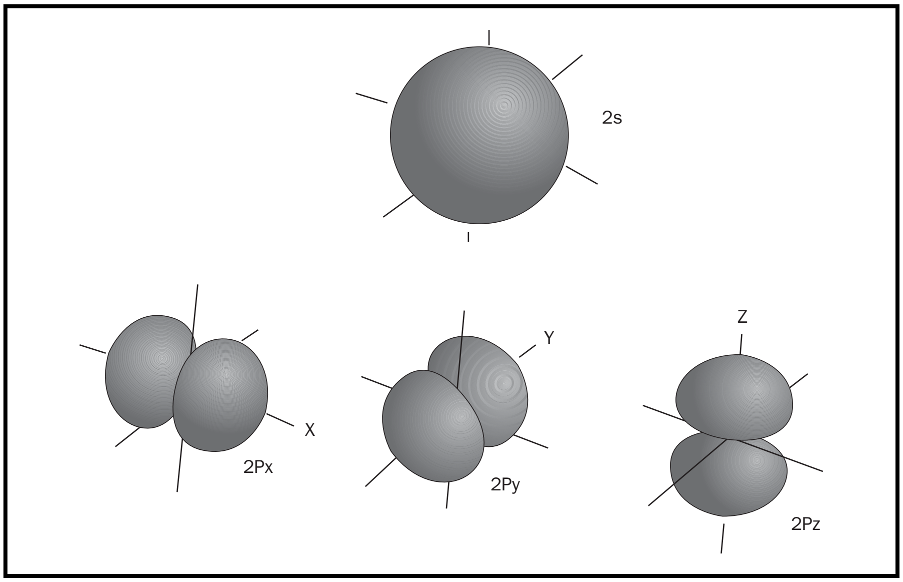


Figure 6. Shapes of atomic orbitals: s, p_x, p_y, and p_z.

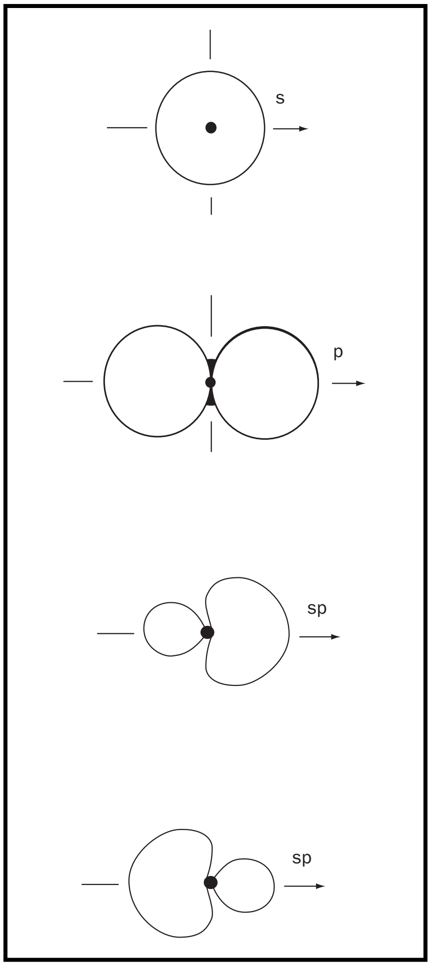


Figure 7. Formation of two sp hybrid orbitals resulting from the combination of one s and one p atomic orbital.

phase: homogeneous state of matter consisting of gases, liquids, or solids

The sp^3 hybrids about the C atom are used to form the four bonds in diamond, methane, and all alkanes. The sp^2 hybrids are used to form the double bond in all alkenes. The sp hybrids are used in the triple bond in acetylene. The shapes of the molecules of the simple gases ethane, ethylene, and acetylene are well described by the hybrid model. (See Table 3.)

All three compounds burn in air. Acetylene is used for welding; ethylene is polymerized to give polyethylene, a plastic common in every kitchen.

Coordinate Bond

Molecules, such as ammonia, that have a lone pair of electrons are able to donate these two electrons to an empty orbital on a metal atom, to form a coordinate or dative bond. A typical example is the deep blue coordination complex of copper, $[Cu(NH_3)_4]2+$, which has four Cu(N bonds in a square plane.

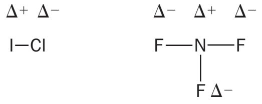
Similarly, a proton will attach itself to the lone pair of electrons on the ammonia molecule to give the tetrahedral NH_4^+ ammonium cation. The lone pair on the N atom in $N(CH_3)_3$ will bond to the empty orbital on the B atom in $B(CH_3)_3$ to give the compound $(CH_3)_3N{-}B(CH_3)_3$.

The F^- anion will donate a pair of electrons to the B atom in the BF_3 molecule to form the tetrahedral BF_4^- anion. This type of bonding where one atom, the donor, supplies both electrons to form the bond to the second atom, the acceptor, is termed Coordinate, or sometimes Dative.

Van der Waals Attractions

Materials held together by van der Waals attractions often have a smell at room temperature (e.g., camphor and menthol). This is caused by the molecules escaping from the solid and subliming directly into the gas **phase**. The attractive forces between the molecules are weak. These forces arise from distortions in the electron cloud around the molecule, which cause some parts to be relatively positively charged, while other parts are relatively negative.

Polar bonds. When a covalent (electron pair) bond is formed between two different atoms, the pair of electrons is concentrated nearer the atom with the larger power to attract electrons. This power is termed electronegativity. The charge asymmetry generates a bond moment. For example,



$$\overset{\Delta+}{I}{-}\overset{\Delta-}{Cl} \qquad \overset{\Delta-}{F}{-}\overset{\Delta+}{N}{-}\overset{\Delta-}{F},\ \text{N}{-}F\ \Delta-$$

Table 3. Physical properties of three simple hydrocarbons.

PHYSICAL PROPERTIES OF THREE SIMPLE HYDROCARBONS

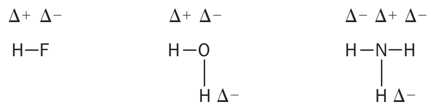
	Ethane	Ethylene	Acetylene
Formula	$H_3C{-}CH_3$	$H_2C{=}CH_2$	$HC{\equiv}CH$
Molecular mass	30	28	26
Boiling point (°C)	−88.6	−103.7	−84.0
Shape	3H's, part of a tetrahedron about each C	4H's and 2C's coplanar, HCH angle = 120°	H's and C's collinear
C—C bond, orbitals	Single, sigma	Double, sigma + pi	Triple, sigma + two pi

Depending on its shape, the molecule as a whole can have a dipole moment μ. For instance, for BF_3, $\mu=0$ because BF_3 is trigonal planar, while for NF_3, $\mu=0.23$ D, because NF_3 is **pyramidal**. The presence of a dipole moment in a molecule results in attractions between pairs of molecules, termed Keesom forces.

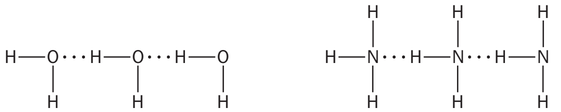
pyramidal: relating to a geometric arrangement of four electron-donating groups located at the four vertices of a pyramid

Polarizability. More interestingly, neutral molecules with a zero dipole moment are mutually attracted to give liquids (such as CCl_4) and solids (such as naphthalene). These attractions, termed London forces or dispersion forces, arise from the ease of distortion of the electron cloud of the molecule as a whole. This is termed polarizability and is related to the volume of the molecule and the number of electrons in the valence shells of the atoms on the exposed surface of the molecule. The net effect (surprisingly, perhaps) is large and accounts for the relatively high melting points of iodine, CO_2 (dry ice), and naphthalene. These London forces are important; they are the attractions between the long-chain polymeric molecules in solid polyvinyl chloride (PVC) and polyethylene.

Hydrogen bonding. The effect of polarity of a covalent bond is magnified in the case of a hydrogen atom bonded to an atom of either fluorine, oxygen, or nitrogen. In simple molecules, the distortion of the electron cloud is large, causing the hydrogen atoms to be slightly positively charged. For instance,



This results in a strong attraction between pairs of molecules:



These strong intermolecular attractions are termed **hydrogen bonds** and, unlike London forces, are directional. They would be represented in the cross-hatched area in Figure 2. It is this intermolecular hydrogen bonding that causes boiling points to be considerably higher than might be expected for molecules with low molecular masses, such as HF, H_2O, and NH_3. (See Table 4.)

Figure 8 compares the boiling points of the series CH_4, SiH_4, GeH_4, and SnH_4 with those of H_2O, H_2S, H_2Se, H_2Te, and the **inert** gases, and it shows the very high boiling point of water. It is these same OH···O hydrogen bonds

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

hydrogen bond: interaction between H atoms and lone pair electrons that constitutes hydrogen bonding

inert: incapable of reacting with another substance

Table 4. Physical properties of simple compounds.

PHYSICAL PROPERTIES OF SIMPLE COMPOUNDS

Compound	CH_4	NH_3	H_2O	HF	SiH_4	PH_3	H_2S	HCl
Molecular mass	16	17	18	20	32	34	34	36
Boiling Point (°C)	−161	−33	+100	+20	−111	−88	−60	−85
μ (D)	0	1.46	1.84	1.82	0	0.58	0.97	1.08

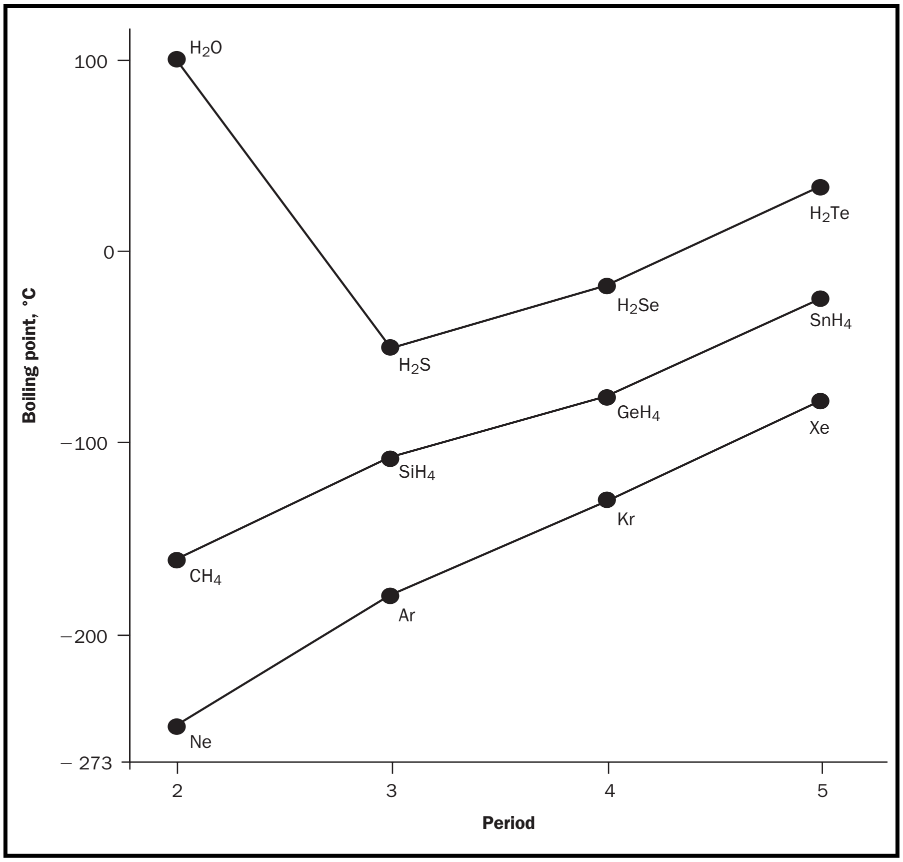


Figure 8. Plot of the boiling points of simple molecules MH_x, versus the position of M in the Periodic Table.

that hold water on a cotton facecloth and that are the forces between the base pairs in the **DNA** in our bodies.

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

Intermediate Cases

There are many homogeneous materials in which the bonding cannot be described simply as one of the four extreme types. The bonding in these materials is intermediate in character. For example, tin at room temperature is metallic in nature, but on cooling, it totally changes its electronic structure and adopts the diamond structure. A small change in energy nudges the tin atoms over the edge as the bonding teeters on the brink between metallic and covalent. It was this change that caused the tin buttons on the great coats of the soldiers of Napoleon's *Grande Armée* to crumble, during the terrible retreat from Moscow in the winter of 1812.

The element gallium is not truly metallic. In the solid, each gallium atom has one short bond of covalent character, and six other much longer contacts to neighboring atoms, intermediate in character between metallic and van der Waals, similar to the structure of crystalline iodine. The six intermediate types of bonding are not easy to describe, but in fact they are often the most important and certainly are very interesting.

Alloys. Many alloys have structures in which the atoms of the different metals are ordered. Hence they behave like compounds (e.g., $AuCu_3$ and Cu_5Zn_8). CsAu has the NaCl structure (see Figure 3) and behaves almost as if it were ionic, $Cs^{+}Au^{(}$. This corresponds with the low ionization energy of Cs, 376 kilojoules per mole, and the favorable electron affinity of Au, 223 kilojoules per mole. CsAu's bonding would lie along the metal/ionic edge of the tetrahedron of bonding types.

Semiconductors. Semiconducting materials are of great practical importance in electronics. Ge, GaAs, ZnSe, and CuBr, are examples and they have bonding that can be described as intermediate between ideal covalent and ideal ionic. Each atom is bonded to four others in a tetrahedron, the zinc blende structure.

Silicate minerals. The bonding within a solid is always reflected in its physical properties, and this relationship to its internal structure is beautifully displayed in the morphology of the series of silicate minerals: quartz, mica, and asbestos. In quartz there is a three-dimensional network of Si—O bonds. In mica there are negatively charged infinite sheets consisting of a two-dimensional network of SiO_4 units, with the sheets linked by cations. In asbestos, there are infinite negatively charged chains of tetrahedral SiO_4 units with strong covalent Si—O—Si bonds. The chains are attached to each other via cations. These latter two solids are each held together by two types of bonds, and the difference between the very strong covalent bonding and the other weaker attractions is evident: Mica is easily split into sheets, whereas asbestos consists of fibers.

Glass. Ordinary glass is an amorphous solid, constructed of negatively charged fragments of nets of SiO_4 units that are linked by Na^+ and $Ca2^+$ cations. There is no internal order. As a result, glass shatters to give curved surfaces; and it gradually softens on heating and does not have a sharp melting point. The bonding in ceramic materials (such as bricks, tiles, pottery, and insulators) is similar, predominantly ionic.

Conclusion

It is important to remember that bonding is always accompanied by a reduction in energy, and that all bonding theory is but an intellectual model, a mental scaffolding on an atomic scale, on which to hang our ideas in hopes of giving a self-consistent explanation of observed reality. SEE ALSO MOLECULAR ORBITAL THEORY; VALENCE BOND THEORY.

Michael Laing

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5
B
BORON
10.8115

Boron

MELTING POINT: 2,300°C
BOILING POINT: 2,550°C
DENSITY: 2.46g cm^3
MOST COMMON IONS: B^{3+}

Boron occurs in nature as part of oxygenated compounds, or borates, that have been known since ancient times for their use in glass and metal production. In 1808 Joseph-Louis Gay-Lussac and Louis Jacques Thenard of France and Humphry Davy of England discovered the element boron almost concurrently. Another century passed before boron was successfully isolated in pure form. Elemental boron in its amorphous form is a dark brown powder; it is a yellowish-brown, hard, brittle solid in its **monoclinic** crystalline form. It melts at 2,300°C (4,172°F). Boron is unreactive to oxygen, water, acids, and alkalis. Boron compounds burn yellow-green during the flame test.

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

There are 217 minerals that contain the element boron but few are found in great enough quantities to make them commercially valuable. The few that are found in some quantity are white in color. Some boron-containing minerals, their percentages of boron, and the countries of their production in 2000 are: colemanite (51%), the United States and Turkey; datolite (25%), Russia; kernite (51%), Turkey and the United States; probertite (50%), Turkey and the United States; tincal (36%), Argentina, Turkey, and the United States; and ulexite (53%), Argentina, Bolivia, Peru, Turkey, and the United States. From these minerals, chemical compounds such as borax (sodium borate) and boric acid of various grades are manufactured. These compounds are clear or white. Commercial products, in order of the total quantity of boron consumed, are: fiberglass, borosilicate glass, soaps and detergents, fertilizers, enamels, fire retardants, and **alloys**.

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

Sodium borohydride is marketed in powdered or pellet form, and in solution, for use in fuel cells. Boron nitride can withstand temperatures of up to 650°C (1,202°F); when subjected to high pressures and temperatures, it forms cubic crystals whose hardness rivals that of diamond. Boron carbide, produced by reacting coke and boric acid at 2,600°C (4,712°F), is a highly refractory material and one of the hardest substances known. It has both abrasive and abrasion-resistant applications, and is used in **nuclear** shielding. SEE ALSO Davy, Humphry; Gay-Lussac, Joseph-Louis; Nuclear Chemistry.

nuclear: having to do with the nucleus of an atom

Phyllis A. Lyday

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Boyle, Robert

BRITISH PHYSICIST AND CHEMIST
1627–1691

Robert Boyle was born in 1627, the youngest son of a large upper-class English family with significant landholdings in Ireland and ties to both sides of the English Civil War (1642–1651). Boyle's literary and religious interests

British physicist and chemist Robert Boyle (r.) and Denis Papin (l.) inspect Papin's steam digester.

turned to **natural philosophy** as early as 1647. Boyle was active within the Baconian group called "the Invisible College," which would later become the **Royal Society**, chartered by King Charles II after the Restoration.

Among Boyle's earliest scientific work were studies involving the air pump. At the time, Robert Hooke was Boyle's laboratory assistant. Starting with the German physicist Otto von Guericke's description of an air pump, Hooke improved on its design, reducing its size and increasing its performance while making it easier to use. Utilizing this improved air pump, Boyle devised experiments to explore the properties of air. He examined the behavior of sound, heat, light, electricity, magnetism, chemical reactions (such

natural philosophy: study of nature and the physical universe

Royal Society: The U.K. National Academy of Science, founded in 1660 as a flame), and living systems (such as small animals or plants) in a vacuum. He also considered the behavior of the air itself under extension or compression. The result of this study was the relationship now known as Boyle's law, which states that the pressure and volume of a confined air (gas) are inversely related. Mathematically, this is expressed as pressure times volume equals a constant

$$PV = \text{constant}$$

In 1661 Boyle published the first edition of *The Sceptical Chymist.* A second, expanded edition was published in 1680. It has earned him the title "the father of chemistry" among some British historians. Many point to this as the work in which Boyle examined numerous alchemical procedures and ultimately rejected the classically derived notion of the four elements (earth, air, fire, and water); also dismissed the Paracelsian notion of three essences: salt, sulfur, and mercury; and articulated a relatively modern working definition of atoms. Modern scholarship has questioned some of the details of this interpretation of Boyle's work, but his importance cannot be denied.

metallurgy: the science and technology of metals

alchemy: medieval chemical philosophy having among its asserted aims the transmutation of base metals into gold

Boyle was among the first chemists not primarily trained in medicine and medicinal chemistry, in mining and **metallurgy**, or interested in those applications. He was also among the first to recognize chemistry as an intrinsically important subject for natural philosophy. In pursuing such a line of thought, he had to convince natural philosophers that chemistry was something other than the disreputable **alchemy** it was known as and chemists that the experimental principles of natural philosophy might offer them a valuable area of practice.

reagent: chemical used to cause a specific chemical reaction

Boyle refocused the study of chemistry in two important ways. First, he shifted attention away from questions surrounding the source and history of a material to its identity and purity. Second, he redirected the interest in desired byproducts to an examination of the chemical reaction itself. In doing this, Boyle promoted the use of chemical identity tests and a control arm in an experiment. Among the measures of identity and purity were color, specific gravity, crystal shape, flame tests, solubility, precipitates, and reaction to standardized **reagents**. In these ways, Boyle helped frame the important questions for succeeding chemists until the seminal work of Antoine-Laurent Lavoisier. SEE ALSO ALCHEMY.

David A. Bassett

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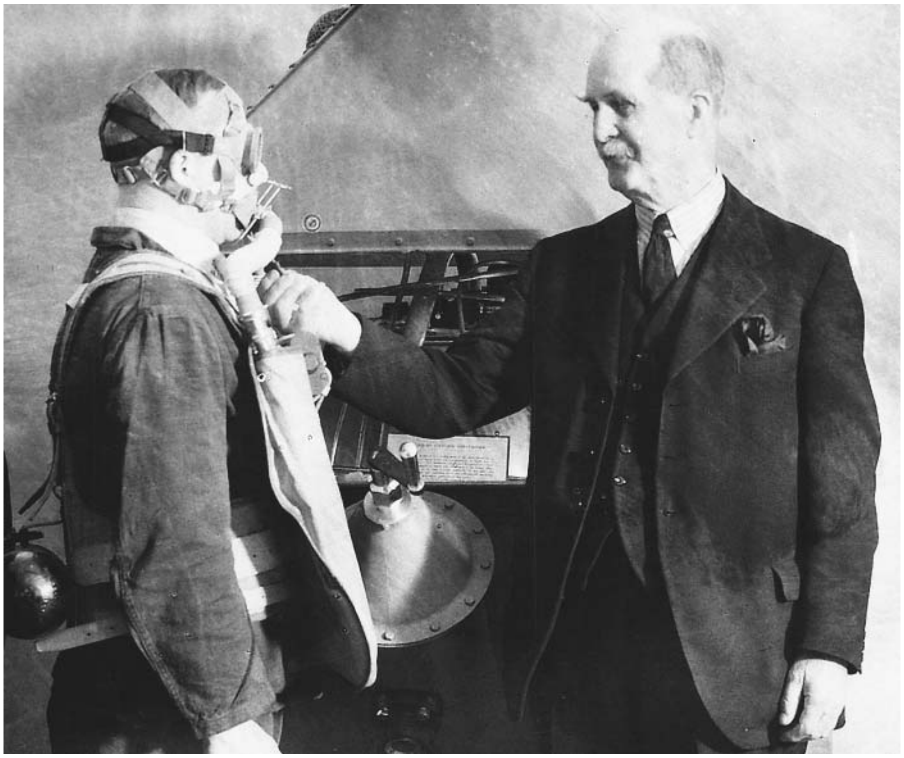
Bragg, William Henry

ENGLISH PHYSICIST
1862–1942

Sir William Henry Bragg was born on July 2, 1862, near Wigton in the northwest of England, the son of an officer in the merchant navy. He attended King William's College on the Isle of Man, before studying for the mathematical degree at Trinity College, Cambridge, in 1884. Two years later he



English physicist Sir William Henry Bragg examining liquid oxygen at a 1936 science exhibition.

was appointed professor of mathematics and physics at the University of Adelaide in South Australia. It was not until nearly twenty years later that Bragg began serious scientific research, concentrating first on **α-particles** and then x rays, in which he was critical of certain aspects of the then accepted theories on both. The significance of his work was such that it warranted his return to England, where he was appointed professor of physics at the University of Leeds in 1909. In 1912 to 1913, working with his son William Lawrence Bragg, a research student at the Cavendish Laboratory, Cambridge, he discovered how to use x rays to determine the molecular structure of crystals. This turned out to be one of the key scientific discoveries of the twentieth century for which the two shared the Nobel Prize for physics in 1915.

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

During World War I, Bragg moved to University College, London, and worked for the admiralty, developing the submarine detection systems ASDIC (Allied Submarine Detection Investigation Committee) and SONAR (Sound Navigation and Ranging). After the war Bragg became disenchanted with University College, and following the death of James Dewar in 1923, he moved to the Royal Institution. There Bragg created a major British center for x-ray crystallography. The scientists at the laboratory established a distinctive approach to x-ray crystallography that later formed the basis of the British school of molecular biology. Bragg trained such figures as Kathleen Lonsdale, the first woman fellow of the **Royal Society**), J. D. Bernal (who went to Birkbeck College), W. T. Astbury (University of Leeds), and, of course, William Henry Bragg's son, (William) Lawrence Bragg. The Braggs came to a tacit agreement that the work in the Royal Institution would concentrate on organic crystals, whereas Lawrence's independent efforts would explicitly focus on minerals.

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

Bragg, knighted for his work during World War I, played a major role in scientific popularization and administration during the interwar period. He was one of the earliest scientists to take advantage of the new medium of radio that he used to full effect to emphasize the value of science for society at large and for industry in particular. From 1935 to 1940 he served as president of the Royal Society, in which capacity he played a major role in helping scientists fleeing from fascist regimes to find employment, in establishing the committee that became the scientific advisory committee to the war cabinet, and in determining what scientific resources would be available for the looming conflict with Germany. During the blitz (the German bombing of London during World War II), the Royal Institution was a designated bomb shelter, and often Bragg would go down to the shelter at night to help boost the morale of people taking refuge there, actions for which he is still remembered. He died, in office, on March 10, 1942. SEE ALSO BRAGG, WILLIAM LAWRENCE; DEWAR, JAMES; LONSDALE, KATHLEEN.

Frank A. J. L. James

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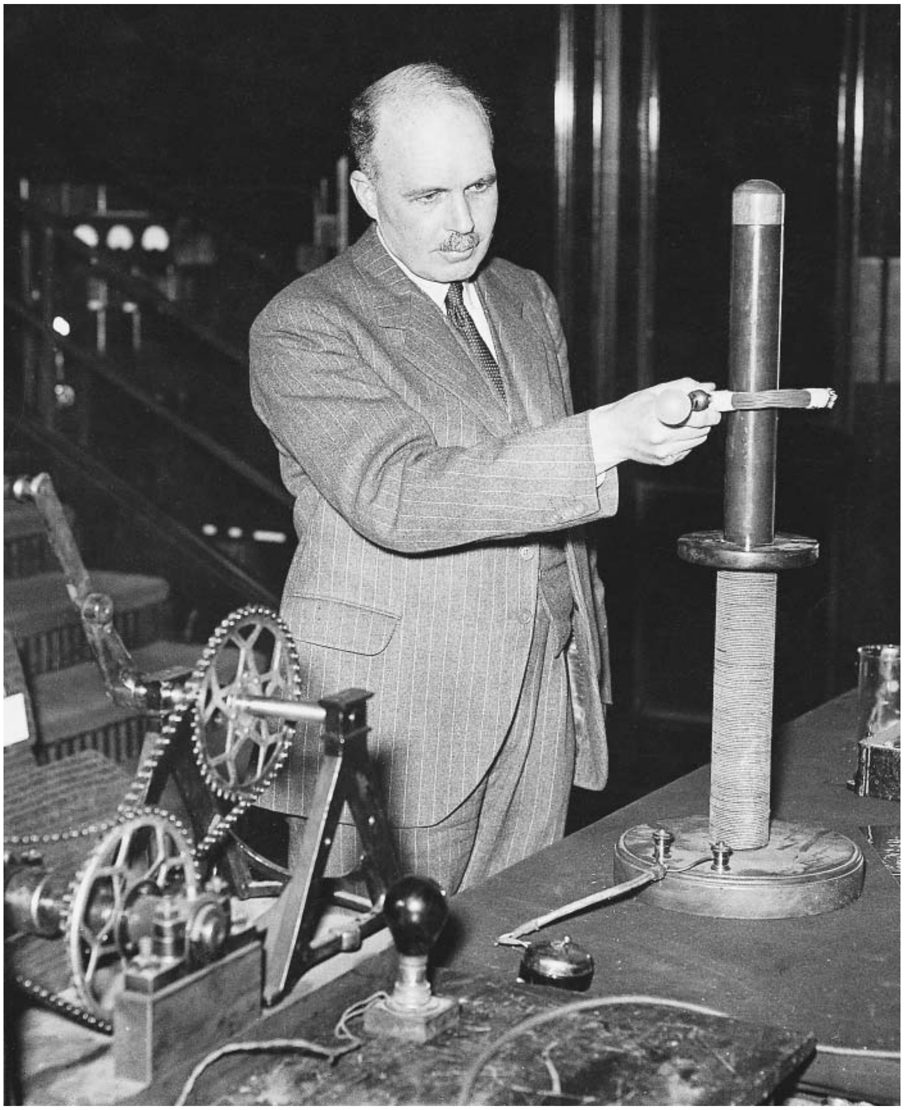
Bragg, William Lawrence

ENGLISH PHYSICIST
1890–1971

Sir William Lawrence Bragg was born on March 31, 1890, in Adelaide, South Australia, where his father, William Henry Bragg, was professor of mathematics and physics. Lawrence attended St. Peter's College, Adelaide, and studied mathematics at the university. The family moved to England in 1909, and Bragg continued his studies at Trinity College, Cambridge, taking first place in the natural sciences degree in 1912. He then began research studies at the Cavendish Laboratory and during 1912 and 1913, in conjunction with his father, he discovered how to use x rays to determine the molecular structure of crystals. Lawrence also determined Bragg's law, $n\lambda = 2d \sin\theta$ the equation that links the wavelength of x rays with the distance between two crystal planes and the angle of incidence. For this work, one of the crucial discoveries of twentieth-century science, the Braggs were jointly awarded the Nobel Prize for physics in 1915; sharing the award at the age of twenty-five, Lawrence remains the youngest-ever winner of the esteemed prize.



English physicist William Lawrence Bragg, co-recipient, with Sir William Henry Bragg, of the 1915 Nobel Prize in physics, "for their services in the analysis of crystal structure by means of X-rays."

During World War I, Bragg served in Flanders in a sound-ranging unit of the Royal Artillery. After demobilization he succeeded Ernest Rutherford as professor of physics at the University of Manchester. There he worked on problems such as the structure of silicates and of **metals**. After briefly directing the National Physical Laboratory, Bragg in 1938 became director of the Cavendish, once again succeeding Rutherford. At the Cavendish, Bragg established a major crystallographical research group despite some opposition from former members of Rutherford's group who wanted the laboratory to continue to concentrate on **nuclear** physics. Bragg held the laboratory together during the World War II years (1939–1945) and served on a number of government scientific committees; as a result of his efforts, he was knighted in 1941.

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

After the war Bragg established at the Cavendish Laboratory, with funding from the Medical Research Council, a unit for the study of molecular structure of biological systems. It was here in 1953 that Francis Crick (whom Bragg did not like) and James Watson determined the double helical structure of **DNA**. At the start of 1954 Bragg moved to the Royal Institution to

DNA: deoxyribonucleic acid—the natural polymer that stores genetic information in the nucleus of a cell try to repair the scientific capacity of the institution after it had been poorly managed by another scientist. Bragg was the only scientist of repute willing to take on this position, and it undoubtedly did him harm within the scientific community, especially the **Royal Society**.

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

Bragg revived the fortunes of the Royal Institution, both by increasing its public programs, especially its schools' lectures, and developing a major research group. This group included Max Perutz and John Kendew, who, working at both the Royal Institution and the Cavendish Laboratory, determined the structures of hemoglobin and myoglobin, for which they won the Nobel Prize for chemistry in 1962. Working with Bragg during the 1960s at the Royal Institution, David (later Lord) Phillips determined the structure of an enzyme, lysozyme, for the first time. On his retirement in 1966, Bragg was able to hand over a Royal Institution now in reasonably good shape to his successor George Porter. Bragg died five years later on July 1, 1971. SEE ALSO Bragg, William Henry; Rutherford, Ernest; Watson, James Dewey.

Frank A. J. L. James

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35
Br
BROMINE
79.9

Bromine

MELTING POINT: **−7.3°C**
BOILING POINT: **59°C**
DENSITY: **3.12 g/cm^3 (liq. at 20°C)**
MOST COMMON IONS: **Br^-, BrO^-, BrO_3^-, BrO_4^-**

Bromine is a member of a family of elements known as **halogens** that are found in group 7A of the Periodic Table. Bromine was discovered in 1826 in Montpellier, France, by French chemist Antoine J. Balard.

halogen: element in the periodic family numbered VIIA (or 17 in the modern nomenclature) that includes fluorine, chlorine, bromine, iodine, and astatine

Bromine is one of two elements (the other being mercury) that is liquid at normal temperatures. As with the other halogens, bromine is very reactive, corrosive, and poisonous. Both the liquid and vapor of bromine are deep red in color. Bromine has a pungent, irritating odor that is the source of the element's name (the Greek word *bromos* means "stench").

Elemental bromine is a diatomic molecule (Br_2). Bromine will combine with most other elements. Reaction with metallic elements leads to salts such as silver bromide (AgBr), in which the bromine atom has a −1 charge and **oxidation** number. Bromine forms many interesting covalent compounds as well, including two oxides: bromine (IV) oxide (BrO_2) and bromine (I) oxide (Br_2O).

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

Bromine is produced commercially from natural brines and from seawater either by electrolysis or with displacement by chlorine, a somewhat more reactive halogen. The concentration of bromine in seawater is approximately 67 parts per million (ppm) by weight; it is found in Earth's crust at an average level of 3 ppm.

Bromine compounds have a variety of uses. Methyl bromide (CH_3Br) is a common agricultural soil fumigant; other bromohalocarbon compounds have been used as refrigerants and fire suppressants. Inorganic bromides are important components of photographic emulsions. Bromine reacts with liquid water to produce hypobromite ion (BrO^-), a powerful bleaching agent. There are also many dyes and pharmaceutical agents that contain bromine. SEE ALSO Halogens.

John Michael Nicovich

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Brønsted, Johannes Nicolaus

DANISH CHEMIST
1879–1947

Johannes Nicolaus Brønsted was a physical chemist whose work resulted in a new theory of acids and bases. He was born in the town of Varde in Jutland (Denmark), where his father was an engineer for the Danish Heath Society. His mother died shortly after his birth. When his father died in 1893, young Brønsted relocated to Copenhagen, where he was admitted to the old Latin school (high school), the Metropolitanskolen. He passed the school's final examinations in 1897.

Brønsted studied chemistry at the University of Copenhagen. He received a master of science degree in 1902 and a doctorate degree in 1908. After receiving temporary appointments at the University of Copenhagen, he became an assistant professor there in 1905, and full professor in 1908. Brønsted studied chemical affinity, electrolytes, **isotope** separation, reaction kinetics, thermodynamics, and acid-base **catalysis**.

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

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

On May 4, 1923, the Dutch chemical journal *Recueuil des Travaux Chimiques des Pays-Bas* (42:718) received a paper from Brønsted on existing concepts of acids and bases. In this paper Brønsted demonstrated how useful it was to define an acid as a proton donor and a base as a proton acceptor. In the Brønsted scheme, acid-base reactions are proton transfer reactions. Every acid is related to a conjugate base, and every base to a conjugate acid. Also in this paper he pointed out that there is an analogy between the proton transfer that is characteristic of acid-base reactions and the electron transfer that is characteristic of **oxidation**-reduction reactions.

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

On January 19, 1923, an article by Thomas Martin Lowry (1874–1936) was published in the English journal *Chemistry and Industry*, in which the idea of proton transfer between acids and bases was launched. In spite of this, Brønsted's theorizing work has been recognized, and the terms Brønsted acid and Brønsted base have had wide usage. SEE ALSO Acid-Base Chemistry.

Ole Bostrup

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Brønsted Acids ***See Acid-Base Chemistry.***

Bunsen, Robert

GERMAN CHEMIST
1811–1899

German chemist Robert Wilhelm Bunsen, the co-developer of the science of spectroscopy.

Robert Wilhelm Bunsen, born in Göttingen, is often identified with the laboratory burner that bears his name. But to think of him only in relation to the Bunsen burner is to do him a disservice. Bunsen contributed widely to the development of many laboratory instruments, some of which helped to dramatically advance chemistry. His most important work was developing several techniques used to analyze chemical substances.

Born into an academic family and well-versed in many disciplines, Bunsen made chemistry his field of choice. After receiving his doctorate at the age of nineteen, Bunsen went on a partially government-funded tour throughout Europe, where he met many chemists and engineers. His travels provided him with a network of contacts that he used throughout his career. Upon his return and after teaching at several universities, he settled into a professorship at the University of Heidelberg in 1852, where he stayed until his retirement in 1889.

arsenic: toxic element of the phosphorus group

Bunsen was an avid experimentalist. He spent much of his time in the laboratory trying to discover the composition of chemical substances. His early research concerned the properties of **arsenic** and its compounds. In particular, the chemical composition of a certain class of chemicals, called cacodyls, was unknown. His experiments showed that cacodyls were oxides of arsenic. But Bunsen's work with arsenic nearly cost him his life—he nearly killed himself through arsenic poisoning and lost the sight in one eye during his experiments with cacodyls.

galvanic: relating to direct current electricity especially when produced chemically

atomic weight: weight of a single atom of an element in atomic mass units (AMU)

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

As his research advanced to the studies of gases and alkali metals, Bunsen recognized the importance of developing new methods to analyze and identify chemical substances. The importance of quantitative analysis was realized in the late eighteenth century. Chemists needed to probe further into a substance's composition in order to help explain the physical world. Bunsen recognized this need and worked to develop new instruments for this purpose. For example, he invented new types of **galvanic** and carbon-zinc electrochemical cells, or batteries, to isolate barium and sodium. He also constructed a new type of ice calorimeter that measured the volume, rather than the mass, of melted water. This allowed Bunsen to measure a metal's specific heat in order to find its **atomic weight**.

Bunsen's most lasting contribution to chemistry though was **spectroscopy**, which he developed in collaboration with the German physicist

Gustav Kirchhoff. Bunsen became interested in analyzing the colors given off by heating chemicals to the point that they glowed. He heard that Kirchhoff was involved in similar work, and in 1854, Kirchhoff joined Bunsen at the University of Heidelberg. When Kirchhoff suggested that they observe the light being emitted from the elements by dispersing the light with a **prism**, the science of spectroscopy was born. When viewed through a prism, they found that the light was broken down into a series of lines, called **spectral lines**. Bunsen and Kirchhoff determined that the light emitted by each substance had its own unique pattern of spectral lines—a discovery that led to the spectroscopic method of chemical analysis.

prism: triangular-shaped material made from quartz or glass used to diffract light

spectral line: line in a spectrum representing radiation of a single wavelength

It was during the process of developing spectroscopy that the Bunsen burner came into being. Bunsen realized that the spectral patterns observed were being contaminated by the light coming from the burner they were using to heat the elements. He modified the burner he was working with by mixing air into the gas before burning in order to obtain a high temperature, nonluminous flame.

Using the new burner, Bunsen and Kirchhoff were able to clearly see the spectra of all the chemicals they were studying. Together, they catalogued the spectra of all the known elements. This aided chemists enormously, because by identifying their spectral patterns, chemists could determine the composition of any unknown substance. In the process of cataloguing the spectra of the elements, Bunsen and Kirchhoff discovered two new elements that they named after the colors of their spectral lines: cesium (blue) and rubidium (red). Using Bunsen and Kirchhoff's new analytical technique and the spectroscope they next developed, many new elements were subsequently discovered. But spectroscopy not only opened the door to the further analysis of earthly substances, the composition of the stars could also now be deduced.

Bunsen was a very modest man, despite being honored by some of Europe's most prestigious scientific institutions. In 1853 he was elected to the Chemical Society in London and to the Academie des Sciences in Paris. He was named a fellow of the **Royal Society** of London in 1858 and received its Copley Medal in 1860. Bunsen and Kirchhoff were together awarded the first Davy Medal in 1877 for their development of spectroscopy.

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

On his retirement in 1889, Bunsen turned his attention to another of his lifelong interests, geology. Bunsen's contributions to chemistry included not just the Bunsen burner, but also many other instruments that allowed the physical world to be seen in new and informative ways. SEE ALSO SPECTROSCOPY.

Lydia S. Scratch

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C, Vitamin *See Ascorbic Acid.*

Cadmium

48
Cd
CADMIUM
112.40

MELTING POINT: 320.9°C
BOILING POINT: 767°C
DENSITY: 8.642 g/cm^3
MOST COMMON IONS: Cd^{2+}

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

Cadmium is a silver-white, malleable **metal** that exists as crystals having the hexagonal close-packed arrangement, and is usually found combined with other elements in mineral compounds (e.g., cadmium oxide, cadmium chloride, cadmium sulfate, and cadmium sulfide). Cadmium dust can ignite spontaneously in air and is both flammable and explosive when exposed to heat, flame, or oxidizing agents. Toxic fumes are emitted when cadmium metal is heated to high temperatures. Cadmium lacks a definite taste or odor. It was discovered as an impurity in zinc carbonate by Friedrich Strohmeyer in Germany in 1817. Most cadmium is obtained as a byproduct of the chemical treatment of copper, lead, and zinc ores, although it is a naturally occurring element in Earth's crust.

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

Industrial uses of cadmium include electroplating and the manufacture of batteries, metal coatings, and **alloys**. Cadmium is also used as a pigment in paints and plastics. Some fertilizers also contain cadmium.

Food and cigarette smoke are the most likely sources of cadmium exposure for the general population. The total daily intake of cadmium from food, water, and air for an adult living in North America or Europe is estimated to be between 10 and 40 micrograms (3.53×10^{-7} and 1.41×10^{-6} ounces). The U.S. Environmental Protection Agency has established oral reference doses for cadmium: 0.0005 mg/kg/day (from water) and 0.001mg/kg/day (from food). The reference dose is the level that may be consumed over a lifetime with minimal risk of adverse effects. Occupational exposure may occur in individuals who work with cadmium or in industries that produce cadmium. About 15 percent of inhaled cadmium is absorbed by the body, whereas 5 to 8 percent is absorbed from the gastrointestinal tract following cadmium ingestion. Cadmium is transported in the blood by hemoglobin, as well as by albumin and other large molecular weight proteins. The half-life for cadmium in the body is about thirty days, with most of the excess cadmium accumulating in the liver and kidneys. Cadmium is **excreted** primarily in the urine.

excrete: to eliminate or discharge from a living entity

Acute toxicity may result from the ingestion of cadmium. Symptoms that follow cadmium ingestion may include abdominal pain, nausea, and vomiting; symptoms that follow inhalation include acute respiratory irritation and/or inflammation. Epidemiologic studies in humans have found associations between cadmium exposure and lung cancer, and between cadmium exposure and prostate cancer. Other evidence of the carcinogenic potential of cadmium has been found in the results of animal studies. SEE ALSO Toxicity.

Ronald Brecher

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Caffeine

Caffeine belongs to the family of heterocyclic compounds known as purines. It has the systematic name 3,7-dihydro-1,3,7-trimethyl-1H-purine-2,6-dione; it is also known as 1,3,7-trimethylxanthine, and 1,3,7-trimethyl-2,6-dioxopurine. Caffeine can be classified as an **alkaloid**, a term used for substances produced as end products of nitrogen **metabolism** in some plants. The chemical formula is $C_8H_{10}N_4O_2$. Caffeine has a molar mass of 194.19 grams (6.85 ounces). It is soluble in water and in many organic solvents, and it appears in pure form as white crystals. Caffeine can be prepared by extraction from natural sources or by **synthesis** from uric acid.

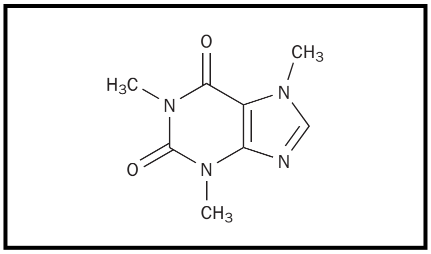

Figure 1. The molecular structure of caffeine.

alkaloid: alkaline nitrogen-based compound extracted from plants

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)

synthesis: combination of starting materials to form a desired product

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

More than sixty plants, including those that give us coffee, tea, cola, and cacao, produce caffeine from the purine xanthine. Whereas caffeine is a natural constituent in coffee, tea, chocolate, and some cola drinks, it is added to consumer products such as soft drinks, diet pills, and **analgesics**. Caffeine is said to be the most widely used drug in the world, and more than 100 million people in the United States consume caffeine each day. It has pharmacological uses: as a cardiac and respiratory stimulant and as an agent that promotes kidney diuresis. A therapeutic dose of caffeine is about the same as the amount found in an average cup of coffee, between 100 and 200 milligrams (0.0071 ounces). Decaffeinated coffee can be prepared through extraction with a solvent (such as methylene chloride), water extraction, or steam extraction.

Caffeine enters the bloodstream about ten minutes after its ingestion and stays in the body for up to twelve hours. Like other alkaloids, caffeine has powerful physiological effects on humans and animals. It stimulates heart muscle and relaxes certain structures that contain smooth muscle, including the coronary arteries and the bronchi. It is a diuretic. Theophylline and theobromine, two other plant alkaloid derivatives of xanthine, have physiological effects similar to those of caffeine.

Caffeine acts as a stimulant of the central nervous system (CNS) through several proposed mechanisms. The most important seems to be its interference with the ability of the neurotransmitter adenosine to bind to its nerve cell **receptor**. Also, caffeine inhibits the enzyme cyclic nucleotide phosphodiesterase, which breaks down intracellular cyclic adenosine monophosphate (cAMP), another messenger involved in the transmission of nerve signals from hormones originating outside the central nervous system

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

Coffee drinks are among the most popular sources of caffeine, believed to be the most commonly used drug worldwide.

such as epinephrine and glucagon—hormones that initiate the “fight or flight” response in animals. Other proposed mechanisms have to do with effects on CNS intracellular calcium ion concentrations.

Caffeine is moderately habit-forming, but because caffeine users can usually control its use, it is not listed as an addicting stimulant by the American Psychiatric Association. Caffeine is not regarded as being harmful to the average healthy adult. In fact there are beneficial effects to be derived from moderate caffeine intake (about three cups of coffee per day). It relieves tiredness, improves thought processes, increases alertness, and enhances physical performance. It may be used to treat respiratory depression and, because it constricts blood vessels in the brain, is often an ingredient in headache remedies. There is some evidence that caffeine may help to mitigate symptoms of migraine headache and lower the risk of gallstones. Some studies show that caffeine may protect against Parkinson’s disease, perhaps by inhibiting the depletion of the neurotransmitter dopamine in brain cells.

There may be some adverse effects due to excessive caffeine intake, such as restlessness, headaches, heart palpitations, heartburn, and insomnia. Some individuals may have a toxic reaction to it. Ingestion by pregnant women and nursing mothers may have adverse effects on fetuses and babies; caffeine crosses the placenta and gets into breast milk. Caffeine has a wide margin of safety. A lethal dose for most people would be the amount of caffeine found in about one hundred cups of coffee.

Some investigations into caffeine-related health issues are inconclusive. Studies have shown no correlation between caffeine intake and increased risk of osteoporosis or increased risk of spontaneous abortion. There is no conclusive evidence linking caffeine intake (as coffee) with bladder, pancreatic, breast, or colon cancer. There is also no conclusive evidence that moderate caffeine intake contributes to heart disease or heart arrhythmias; however, one study has shown that relatively high coffee consumption elevates blood levels of homocysteine (an amino acid)—a situation that may contribute to heart attack or Alzheimer’s disease. There is continuing controversy over whether heavy caffeine intake increases blood pressure, a woman's risk of developing breast lumps, or the incidence of miscarriage. SEE ALSO Dopamine; Epinephrine; Stimulants.

Sharron W. Smith

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Calcium

MELTING POINT: 839°C
BOILING POINT: 1,484°C
DENSITY: 1.55 g/cm^3
MOST COMMON IONS: Ca^{2+}

20
Ca
CALCIUM
40.08

Calcium is the fifth most abundant element in Earth's crust, with calcium oxide, CaO (lime), being among the most common of all terrestrial compounds. Calcium is very important from a biological standpoint, being critical to bones, teeth, and shells of various animals, most often appearing in the form of insoluble calcium phosphate, $Ca_3(PO_4)_2$. Thus calcium is an important part of a healthy diet.

This worker is spraying a lake in Sweden with agricultural lime (calcium oxide), in an attempt to counteract the inflow of acidic materials.

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

In elemental form, calcium is a relatively soft, silvery **metal**. Like other alkaline earths, it is too reactive to be found as a free element in nature. It was not until 1808 that Sir Humphry Davy isolated it by doing electrolysis on a mixture of lime (CaO) and mercuric oxide. Calcium's name comes from the Latin word *calx*, which means lime, a substance used since ancient Roman times in various ways, including as plasters for construction.

In addition to its biological role, calcium's presence is widespread in both nature and industry. As lime, it has many important commercial uses including in the treatment of drinking water and in the production and purification of iron and lead. Because of its usefulness, global consumption of lime exceeds 100 million tons annually. Other calcium compounds include calcium carbonate ($CaCO_3$), which is better known as limestone and is the principal component of stalactites and stalagmites in underground caves. Because it is a weak base, calcium carbonate is also used as an antacid. Calcium silicates (Ca_2SiO_4 and Ca_3SiO_5) are major ingredients in Portland cement, named because it resembles natural calcium minerals found on the Isle of portland in England. Calcium chloride ($CaCl_2$) is an excellent deicing and drying agent. In short, calcium is a very important and useful element. SEE ALSO ALKALINE EARTH METALS; DAVY, HUMPHRY.

David A. Dobberpuhl

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Caldwell, Mary

AMERICAN BIOCHEMIST
1890–1972

During the early part of the twentieth century, women were rarely able to find a career related to chemistry. However, there were three particular fields that were havens for women: crystallography (to which physicist Dorothy Hodgkin contributed); radioactivity (a field that physicist Lise Meitner and chemist Marie Curie excelled in); and biochemistry, where Mary Caldwell was able to pursue a lifelong career.

Caldwell was born in 1890 in Bogota, Colombia, to American parents. Her parents strongly supported the concept of higher education, and all five children in her immediate family became scholars or educators. In the United States, women's colleges were a major avenue for young women to obtain a degree, and Caldwell attended Western College for Women in Oxford, Ohio. She received a B.S. in 1913 and was hired by the same institution as an instructor the following year. In 1917 she was promoted to the rank of assistant professor. Caldwell remained only one more year at Western College, deciding that she needed to acquire more specialized knowledge if she was going to follow her dreams.

In 1918 Caldwell entered Columbia University, in New York, from which she received an M.S. in 1919 and a Ph.D. in 1921. Caldwell was so talented that she was immediately hired by Columbia as an instructor. The only woman in a department at a time when the very idea of women serving as chemistry faculty was almost totally unheard of beyond women's colleges, she rose through the ranks to full professorship in 1948.

Besides carrying a heavy teaching load, Caldwell developed a strong research program in nutrition and biochemistry. Her particular interest was the amylase family of enzymes. Enzymes dramatically speed up the rate at which chemical reactions occur in biological systems. Without enzymes, the complex human body would be unable to function. The amylase enzymes are those that break down starch into sugars; Caldwell's specific interest was pancreatic amylase, the version of the enzyme present in the mammalian pancreas. When she started her research, she was dissatisfied with the purity of the then commercially available enzyme. Over the next two decades she developed methods for producing pure crystalline amylase. Today, purified amylases are used in industry for fermentation, for wallpaper sizing, and in preprepared foods.

The methods Caldwell developed were applicable to other enzymes, and they were used by laboratories in the United States and Europe as a general enzyme purification procedure. Having isolated the pure enzyme, subsequent research in her laboratory showed for the first time that amylases were proteins.

Caldwell served as an important role model for aspiring women chemists. At a time when there were very few women chemists, she encouraged her women students to further pursue their education and research and become chemists and biochemists themselves. She retired in 1959, and the following year she was awarded the Garvan Medal by the American Chemical Society. This medal was awarded to a woman chemist for outstanding achievement, and for Caldwell, receiving the medal was the high point of her life. Outside of her work, she was an avid hiker until a muscular disease afflicted her. She died in Fishkill, New York, in 1972. SEE ALSO Curie, Marie Sklodowska; Enzymes; Hodgkin, Dorothy; Meitner, Lise; Radioactivity.

Marelene Rayner-Canham
Geoffrey W. Rayner-Canham

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Californium

MELTING POINT: **900°C**
BOILING POINT: **Unknown**
DENSITY: **Unknown**
MOST COMMON IONS: **Cf^{2+}, Cf^{3+}**

98
Cf
CALIFORNIUM
252

Element 98, named after the state of California, was first synthesized by the research group of Glenn Seaborg in 1950 at the University of California at

The radioactive element californium is used in airport x-ray equipment.

Berkeley. A target of microgram amounts of an **isotope** of curium (^{242}Cm) was bombarded with accelerated helium ions in a cyclotron, to produce approximately 5,000 atoms of a californium isotope of mass 245 and a half-life of 44 minutes.

Californium, like all the actinide elements heavier than plutonium, exists in a stable trivalent **oxidation** state in **aqueous solutions**. It has also been found to exist in the (less stable) **tetravalent oxidation state** in solution. The ground state electronic configuration for the atom is $5f^{10}7s^2$. Metallic californium has a face-centered cubic structure near its melting point and a double hexagonal close-packed structure at temperatures below its melting point. Californium has eighteen isotopes, all of which are radioactive. The longest-lived isotope has a mass number of 251 and a half-life of 900 years. The isotope having mass number 252 and a half-life of 2.65 years undergoes **radioactive decay**, a fraction of which (3%) is via spontaneous **nuclear fission**; it releases neutrons in the fission event. Californium-252 has been used as a neutron source in a variety of analytical techniques, in medical diagnostic tests that require **activation analysis**, and in the production of short-lived nuclides. Californium neutron sources are used to image low density materials (especially hydrogenous materials). The compactness and portability of ^{252}Cf neutron sources has resulted in their use in such areas as the detection of **metals** in deep wells, lunar exploration, and nuclear weapons monitoring. SEE ALSO ACTINIUM; BERKELIUM; EINSTEINIUM; FERMIUM; LAWRENCIUM; MENDELEVIUM; NEPTUNIUM; NOBELIUM; PLUTONIUM; PROTACTINIUM; RUTHERFORDIUM; SEABORG, GLENN THEODORE; THORIUM; URANIUM.

Gregory R. Choppin

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

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

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

tetravalent oxidation state: bonding state of an atom that can form four bonds

radioactive decay: process involving emission of subatomic particles from the nucleus, typically accompanied by emission of very short wavelength electromagnetic radiation

nuclear: having to do with the nucleus of an atom

fission: process of splitting of a heavy atom into smaller pieces

activation analysis: technique that identifies elements present in a sample by inducing radioactivity through absorption of neutrons

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

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Calvin, Melvin

AMERICAN CHEMIST
1911–1997

Melvin Calvin was born to immigrant parents on April 8, 1911, in St. Paul, Minnesota. Calvin's family subsequently moved to Detroit, where young Calvin attended high school. With the help of a scholarship he attended the Michigan College of Mining and Technology (now Michigan Technological University) during the years 1927 to 1931 as its first chemistry major. He received a bachelor of science degree in 1931. Because offerings in chemistry were few, he took courses in disciplines such as mineralogy, geology, paleontology, and civil engineering, which helped him in his later interdisciplinary research.

Calvin continued his studies at the University of Minnesota, where he investigated the electron affinities of **halogen** atoms. He received a Ph.D. degree in 1935. As a Rockefeller Foundation fellow at the University of Manchester in England (1935–1937), Calvin worked with Michael Polanyi, who introduced him to the interdisciplinary approach, on coordination **catalysis**, the activation of molecular hydrogen, and metalloporphyrins. In 1937 he joined the faculty of the University of California, Berkeley, as an instructor, and remained there for the balance of his career.

halogen: element in the periodic family numbered VIIA (or 17 in the modern nomenclature) that includes fluorine, chlorine, bromine, iodine, and astatine

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

During the early 1940s Calvin worked on molecular genetics. He proposed that **hydrogen bonding** was involved in the stacking of nucleic acid bases within chromosomes. During World War II he produced an oxygen-generating apparatus that used cobalt complexes that bond reversibly with oxygen, for use in submarines and on destroyers. As a member of the **Manhattan Project**, he used chelation and solvent extraction to purify and **isolate** plutonium from the **fission** products of irradiated uranium.

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

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

isolate: part of a reaction mixture that is separated and contains the material of interest

fission: process of splitting an atom into smaller pieces

In 1942 Calvin married Genevieve Jemtegaard. After their first child Elin's death, related to Rh factor incompatibility, Calvin and his wife were part of an interdisciplinary project that investigated the etiology of the disease. They helped to determine the composition and structure of the Rh factor, named elinin for their daughter.

In 1946 Calvin began to investigate **photosynthesis**. He added carbon dioxide containing the radioactive **isotope** carbon-14 (as a tracer) to a suspension of the single-celled green alga *Chlorella pyrenoidosa*. By stopping the plant's growth at various stages and then isolating and identifying the radioactive compounds (present in minute amounts), he determined most of the reactions that comprise the intermediate steps of photosynthesis, by which carbon dioxide is converted into carbohydrates. He found that the so-called dark reactions of photosynthesis (now known as the Calvin cycle) is driven by compounds produced in the "light" reactions, which occur as a result of the absorption of light by **chlorophyll** (producing oxygen). This first use of carbon-14 to elucidate a chemical pathway earned Calvin the Nobel Prize in chemistry in 1961. Using isotopic tracer techniques he also traced the path of oxygen in photosynthesis.

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

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

chlorophyll: active molecules in plants undergoing photosynthesis

When his bioorganic research group outgrew its quarters (at Berkeley), Calvin himself designed the Laboratory of Chemical Biodynamics. His design of a circular building included spacious laboratories, many windows, and few walls. He directed the laboratory until his retirement (1980), at which time it was renamed the Melvin Calvin Laboratory. He died in Berkeley, California, on January 8, 1997, after several years of declining health. SEE ALSO MANHATTAN PROJECT; NUCLEIC ACIDS; PHOTOSYNTHESIS.

George B. Kauffman

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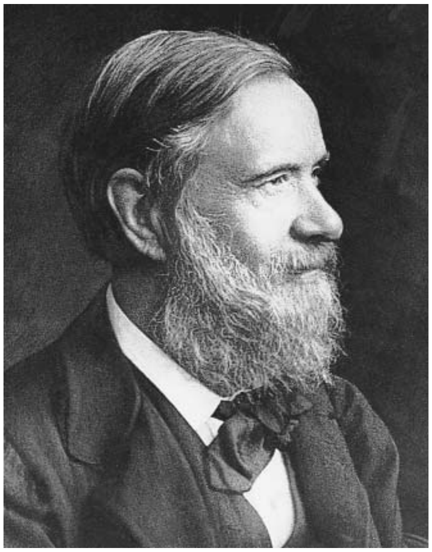
Cancer ***See Carcinogen; Mutagen.***

Cannizzaro, Stanislao

ITALIAN CHEMIST
1826–1910



Italian chemist Stanislao Cannizzaro, known for his theories on atomic weight.

Born in Palermo, Sicily, in 1826, Stanislao Cannizzaro began medical studies at the University of Palermo before moving to Pisa to study chemistry. However, when the Sicilian revolt broke out in 1848, Cannizzaro took part in the capture of Messina. The failure of the revolt forced Cannizzaro to flee to France, where he continued his studies in chemistry at the laboratory of Michel-Eugène Chevreul. In 1851, he returned to Italy and accepted a teaching position in Alessandro.

It was at Alessandro that Cannizzaro completed his studies of the reaction in which the action of alkali on benzaldehyde generates benzoic acid and benzyl alcohol, which came to be known as the Cannizzaro reaction. Further studies on the reaction revealed that it could employ any aldehyde without a hydrogen atom on the carbon closest to the carbonyl group.

Cannizzaro was a talented organic chemist and an early leader in the discipline, but it is his contribution to the then-existing debate over atoms, molecules, and atomic weights for which he is best known. He championed Amedeo Avogadro's notion that equal volumes of gas at the same pressure and temperature held equal numbers of molecules or atoms, and the notion that equal volumes of gas could be used to calculate atomic weights. In so doing, Cannizzaro provided a new understanding of chemistry.

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

During the early 1800s, many chemists were weighing in on **atomic theory** debates, including the debate over the actual, corporeal existence of atoms, with varying degrees of cogency. One difficulty arose from the fact that chemical formulas could be written in any one of a number of ways, if the atomic weights were unknown. For example, the formula for ordinary water, which we know is H_2O, was often written "HO." Use of the latter formula required a belief that oxygen was only eight times as massive as hydrogen, and not sixteen times. The establishment of atomic weights was an important goal of chemists, as all chemical formulas were determined by ratios of elements, leading to empirical and not molecular formulas. Further, some of the leading chemists of the day had their own idiosyncratic theories on how atoms interacted, and there remained the belief that atoms did not actually exist.

In 1858 Cannizzaro published his "Sketch of a Course in Chemical Philosophy" in the journal *Il Nuovo Cimento*, in which he undertook to resolve many of chemistry's outstanding issues, basing his arguments on the work of Avogadro. Cannizzaro felt strongly that a consensus on these issues needed to be achieved. But the paper had little effect at the time of its publication. In 1860 August Kekulé, with the help of Adolphe Wurtz and Carl Weltzien, presided over the first international congress of chemists in Karlsruhe, Germany. Over 140 chemists, including Cannizzaro, attended the three days of discussion and debate. It was the organizers' hope that the congress would resolve some of the aforementioned issues. A participant posed the basic question: "Shall a difference be made between the expressions 'molecule' and 'atom' such that a molecule be named the smallest particle of bodies which can enter into chemical reactions . . . atoms being the smallest particles of those bodies which are contained in molecules?" (DeMilt, p. 38). Cannizzaro was present at the conference and spoke at length on virtually every subject that was debated.

Little was resolved at Karlsruhe. Still, in the words of attendee Dimitri Mendeleev, Jean-Baptiste-André Dumas made a brilliant speech proposing to use the new atomic weights only in organic chemistry, leaving the old for inorganic. Against this Cannizzaro spoke heatedly, showing that all should use the same new **atomic weight**. There was no vote on this question, but the great majority took the side of Cannizzaro.

atomic weight: weight of a single atom of an element in atomic mass units (AMU)

It was after his departure from the conference that Cannizzaro finally made his point and settled the atomic weight debate. Angelo Pavesi, professor of chemistry at the University of Pavia and Cannizzaro's friend, distributed a pamphlet at the conference that contained Cannizzaro's 1858 "Sketch of a Course in Chemical Philosophy." The time was right for those in attendance to at last recognize that a systematic approach to atomic and molecular weights based on the work of Avogadro would resolve many of the outstanding disagreements. The Karlsruhe conference and Cannizzaro's paper are inevitably linked and represent a major turning point in our understanding of chemistry. SEE ALSO Atoms; Avogadro, Amedeo; Chevreul, Michel; Kekulé, Friedrich August, Mendeleev, Dimitri; Periodic Table.

Todd W. Whitcombe

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Carbohydrates

Carbohydrates are the most abundant natural organic compounds on Earth. The term "carbohydrate" derives from their general formula of $C_n(H_2O)_n$, first determined in the nineteenth century, and indicates that these compounds are hydrates of carbon. Carbohydrates are more specifically defined as polyhydroxy aldehydes or **ketones** and the products derived from them. Carbohydrates are synthesized via **photosynthesis** by plants, algae, and some bacteria. Animals feeding on these organisms then use the energy stored in these compounds.

Energy storage is not the only function of carbohydrates. They have a variety of functions in living organisms, including their contribution to the structure of cell walls and their vital role in communication at the site of cell membranes. Carbohydrates form part of the backbone of **RNA** and **DNA** molecules, and they are also found linked to proteins and **lipids** as glycoproteins and glycolipids. The three basic groups of carbohydrates based on size are: **monosaccharides**, oligosaccharides, and polysaccharides (saccharide from the Greek *sakcharon*, or "sugar"). The oligosaccharides and polysaccharides are composed of a few and many monosaccharides, respectively. Monosaccharides have two major groups: the aldoses and the ketoses.

Aldoses

The simplest of the aldoses is glyceraldehyde, which is a triose, or three-carbon sugar. Glyceraldehyde has one chiral carbon and therefore two stereoisomers, designated D and L. In nature, only D sugars occur in abundance. Other aldoses can be derived from glyceraldehyde via insertion of additional hydroxy carbons between the carbonyl carbon and the molecule's other carbons. In this way, tetroses, pentoses, and hexoses are formed. Although glyceraldehyde and the tetroses can occur only as simple linear struc-

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

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

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

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

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

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

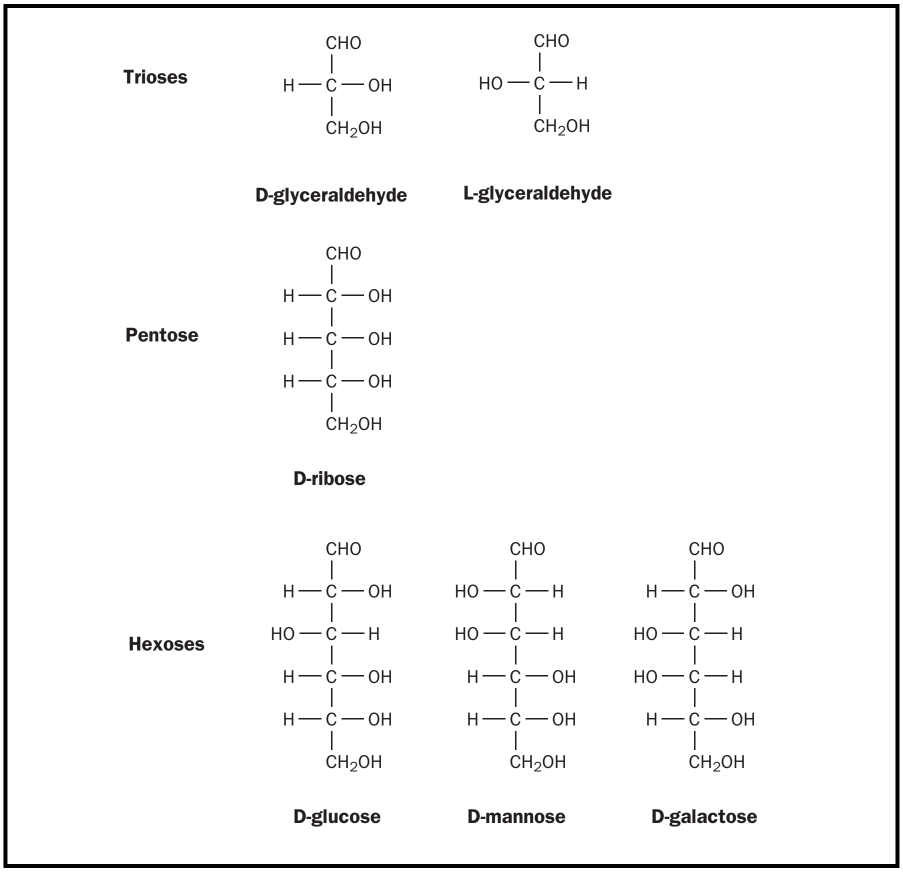

Figure 1. The structure of selected aldoses.

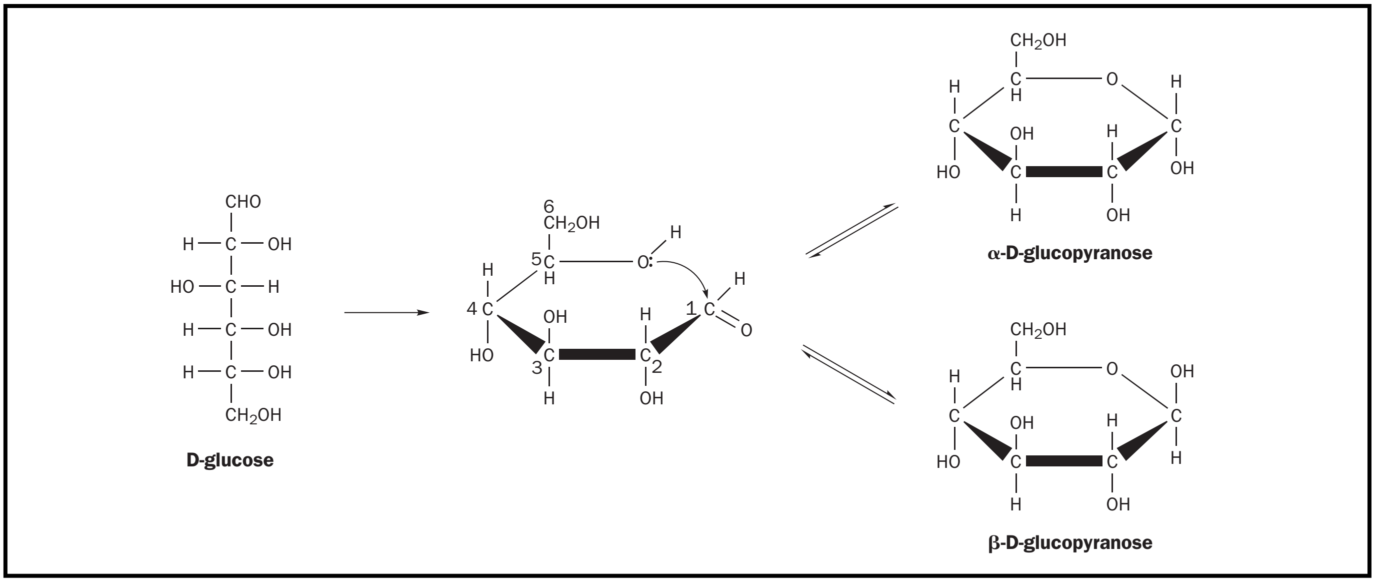

Figure 2. The ring formation of glucose. The rings are shown as Haworth projections.

tures, the pentoses and the hexoses can also form rings. The ring formation has important effects on the properties of these molecules.

Glucose, an aldohexose, is the most common of the monosaccharides. In various combinations and permutations, it forms starch, cellulose, sucrose (table sugar), and lactose (milk sugar), among other things. When metabolized via the glycolytic pathway, it is the major energy source for many living things. Most commonly, glucose forms a ring, its fifth hydroxyl group reacting with the aldehyde carbonyl group to form a **hemiacetal** (see Figure 2). As a result of this reaction, the sugar forms a six-membered ring and the carbonyl carbon becomes chiral. The two new stereoisomers of glucose that revolve on the aldehyde carbon are designated *α* and *β* and are considered anomers of one another. The now chiral carbon is called the "anomeric" carbon. These six-membered ring structures are called pyranoses, as they resemble the compound pyran. Thus, in its ring forms, glucose is properly designated *α*-D-glucopyranose, or *β*-D-glucopyranose.

These pyranose rings are not flat and can assume several different conformations. In general, the most stable conformation is the "chair" conformation, in which the bulky atomic groups (e.g., the hydroxyl and hydroxymethyl groups) are equatorial or within the plane of the ring (see Figure 3). The hydrogens would then be axial or **perpendicular** to the plane of the ring. Only in *β*-D-glucopyranose are all of the bulky groups equatorial; thus, *β*-D-glucopyranose is more stable than *α*-D-glucopyranose, in which the C-1 hydroxyl group is axial to the ring. The *α* and *β* forms of

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

hemiacetal: a compound formed from an alcohol and a carbonyl-containing molecule

perpendicular: condition in which two lines (or linear entities like chemical bonds) intersect at a 90-degree angle

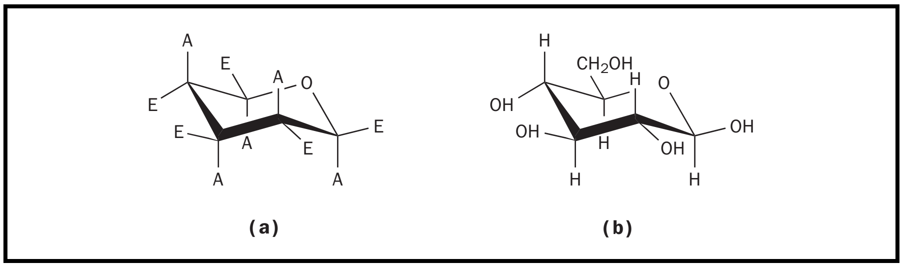

Figure 3. Chair conformations. (a) Axial (A) and equitorial (E) positions of a boat conformation; (b) β-D-glucose in one possible boat conformation.

glucose are freely interconvertible in solution. At equilibrium, a solution of glucose contains about two-thirds α-D-glucopyranose, one-third α-D-glucopyranose, and small amounts of the linear and five-membered ring forms of glucose.

galactose: six-carbon sugar

Other widely occurring aldoses include mannose, **galactose**, and ribose (see Figure 1). Mannose and galactose are, like glucose, aldohexoses and can form six-membered rings. Mannose is an important part of the complex sugars, or oligosaccharides, that attach to proteins in the formation of glycoproteins. Galactose combines with glucose to form lactose or milk sugar. Structurally, each of these sugars differs from glucose only in the stereochemistry that revolves on one carbon: mannose on C-2 and galactose on C-4. Sugars that differ from one another only in respect to the stereochemistry at one carbon are considered epimers of each other. Thus mannose is the C-2 epimer of glucose, and galactose the C-4 epimer. Mannose and galactose are not epimers; they differ from each other in respect to the stereochemistry revolving around two carbons.

Ribose is an aldopentose. It composes the carbohydrate portion of the ribonucleotides that form a cell's RNA. Ribose, like the aldohexoses, can form a ring. However, ribose forms a five-membered ring, called a "furanose" because of its similarity to the compound furan. Once again, there are two possible forms this ring can have: α-D-ribofuranose and β-D-ribofuranose. RNA contains β-D-ribofuranose.

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

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)

Ketoses

There are fewer ketoses than there are aldoses because ketoses have one less chiral carbon. The most prevalent of the ketoses are dihydroxyacetone, ribulose, xylulose, and fructose (see Figure 4). All four of these sugars are important **intermediates** in **metabolism**. Fructose is, along with glucose, part of sucrose or table sugar. Fructose is a ketohexose, and the only one of the four ketoses that can assume a ring structure. Like ribose, fructose forms a five-membered (or furanose) ring and has α and β anomers.

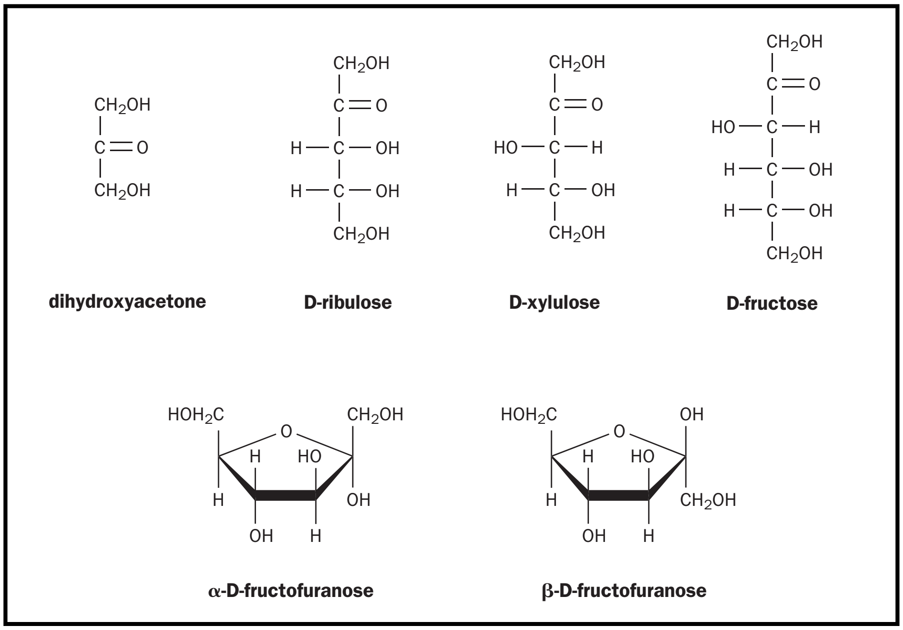

Figure 4. The structures of selected ketoses. Note that dihydroxyacetone does not have a chiral carbon and so does not have D and L variants.

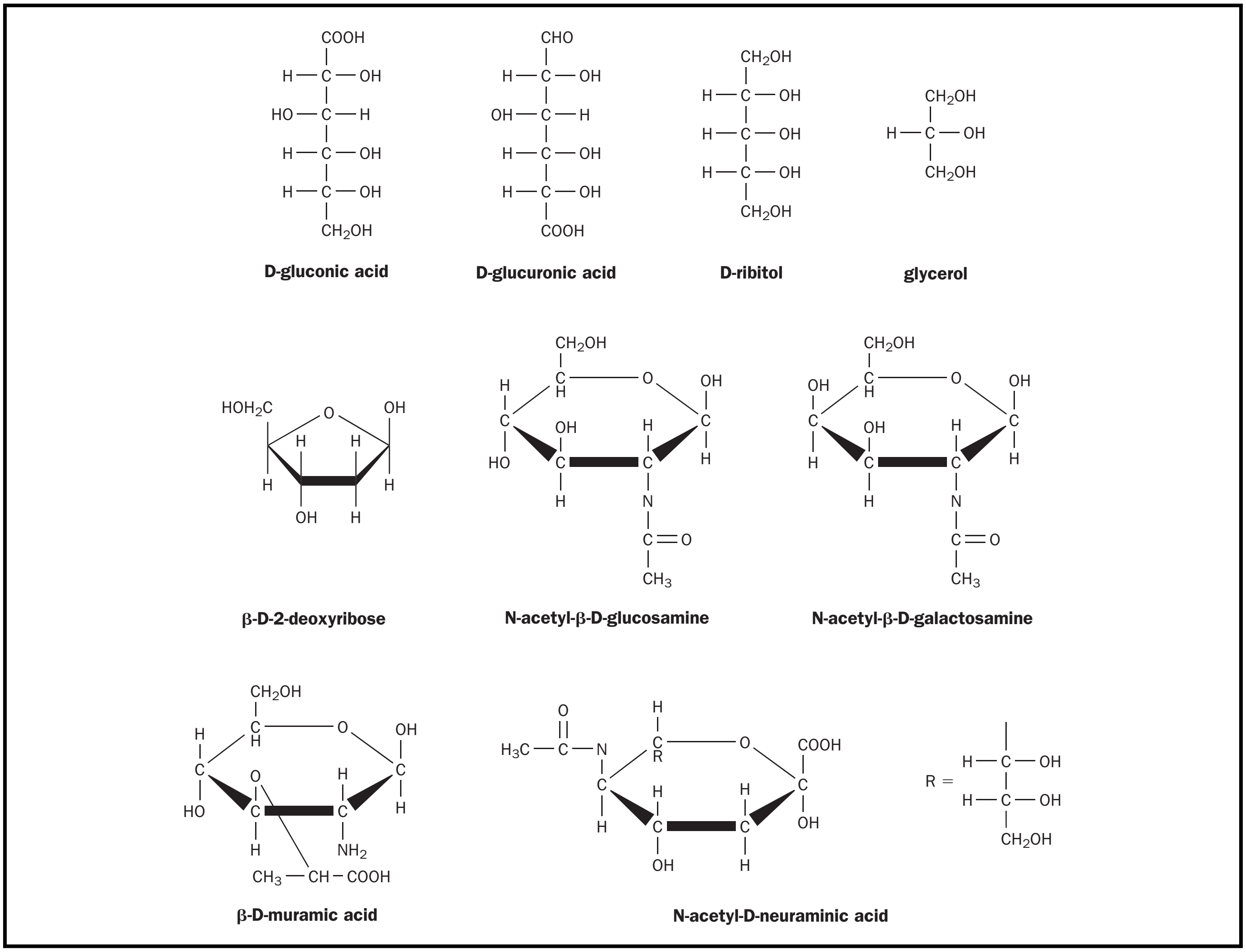

Figure 5. Selected derivatives of monosaccharides.

Monosaccharide Derivatives

Monosaccharides undergo incorporation into oligo- and polysaccharides. Individual monosaccharides can also undergo a variety of transformations. One important modification of monosaccharides is the formation of deoxy sugars. The most biologically significant of the deoxy sugars is β-D-2-deoxyribose (see Figure 5), in which the C-2 hydroxyl group of ribose has been replaced with hydrogen. This deoxy sugar is the sugar component of DNA.

In the amino sugars, an amino group replaces one or more of the hydroxyl groups. The most common of these sugars are D-glucosamine and D-galactosamine, both of which have an amino group in place of the hydroxyl group on the second carbon. Often, these amino groups are acetylated to give N-acetyl sugars, such as N-acetylglucosamine and N-acetylgalactosamine. These sugars are important components of larger polysaccharides. Other important amino sugars are muramic acid and N-acetylneuraminic acid, which are components of the oligosaccharides of glycoproteins and glycolipids, and of bacterial cell walls. Muramic acid and N-acetylneuraminic acid are glucosamines, which have been linked at either C-3 or C-1 to three-carbon acids. Muramic acid is formed via an ether linkage between the C-3 of glucosamine and the hydroxyl group of lactic acid.

N-acetyl-D-neuraminic acid results from the formation of a C–C bond between the C-1 of N-acetyl-D-mannosamine and the C-3 of phosphoenolpyruvate. This and other derivatives of neuraminic acid are collectively called sialic acids and are widely found in bacteria and animals.

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; a compound with the general formula RC(O)OR′

Finally, monosaccharides often form **ester** linkages with phosphate and sulfate ions. In fact it is rare to find free monosaccharide in cells. Glucose is the only unmodified monosaccharide that exists in substantial quantities in living things, in which it exists primarily extracellularly. SEE ALSO CHIRALITY; GLYCOLYSIS.

Stephanie E. Dew

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International Union of Pure and Applied Chemistry. Information available from <http://www.chem.qmw.ac.uk/iupac/>.

Carbon

6
C
CARBON
12.01

MELTING POINT: 3,500°C
BOILING POINT: 4,827°C
DENSITY: 2.62 g/cm^3
MOST COMMON IONS: CO_3^{2-}, HCO_2^-

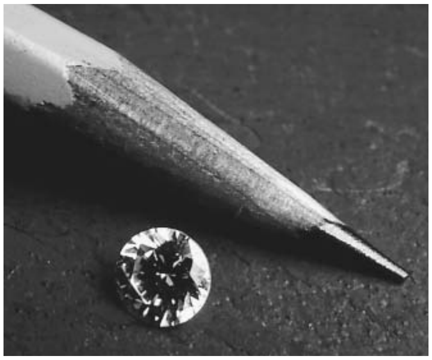
Carbon is the sixth most abundant element in the universe and possibly the most widespread element on earth. Named from the Latin word *carbo*, meaning charcoal, it has been known since ancient times, although not recognized as an element until more modern times. It is found in all living things, but is also commonly found in minerals such as limestone and marble and as a small but important constituent of the atmosphere, as carbon dioxide.

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

biomass: collection of living matter

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

In its elemental form, carbon can be found as diamond, the hardest naturally occurring substance; graphite, an excellent lubricant; or as a fullerene (or "buckyball"). Although five **isotopes** are known, only C-12 (98.9 percent natural abundance) and C-13 (1.1 percent) are stable. Nevertheless, the presence of trace amounts of C-14, a radioactive isotope (with a half-life of 5,730 years), permits "carbon dating" of historical objects.



Diamonds and graphite are allotropes of carbon.

Carbon is unique among the elements in that carbon atoms can form bonds with other carbon atoms. This property, known as "concatenation," is the reason that there are more than several million known organic (containing carbon) compounds.

Carbon is a major constituent of most of our fuels—natural gas, petroleum, coal, wood, and other **biomass**. When burned for their heat content, these fuels produce carbon dioxide, which escapes into the atmosphere. In the "carbon cycle," this carbon dioxide is trapped by plants and reincorporated into useful substances such as cellulose and starch via **photosynthe-**

sis. Since the **Industrial Revolution** of the nineteenth century, which greatly increased the quantity of fuel **combustion**, the concentration of carbon dioxide in the atmosphere has increased. This atmospheric change has been implicated as the cause of global warming.

Carbon is a major constituent of most polymers, both naturally occurring ones such as cellulose, starch, **RNA**, **DNA**, silk, and wool, as well as synthetic ones, including nylon, Teflon, polyethylene, and polystyrene. Some of the strongest and most modern materials replacing **metals** are made of carbon fibers. SEE ALSO Allotropes; Global Warming; Organic Chemistry.

George H. Wahl Jr.

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

combustion: burning, the reaction with oxygen

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

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

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

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Carboxylic Acids ***See Fats and Fatty Acids; Lipids.***

Carcinogen

A carcinogen is a substance that can cause cancer in humans or animals. Carcinogens bring about molecular and biochemical disturbances in cells, resulting in **dedifferentiation** (the loss of cells' morphological and functional specializations, such that they behave like immature cells capable of resuming cell division) and uncontrolled growth (neoplasia).

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

Some common substances that are known to be carcinogenic are asbestos, pesticides, lead, cadmium, **arsenic**, benzene, polyvinyl chlorides (PVC), soot, crystallized silica, glass wool (often a component of fiberglass), tobacco smoke, and smokeless tobacco. Most of these chemical carcinogens are called "procarcinogens," requiring metabolic conversion into "ultimate carcinogens" capable of damaging deoxyribonucleic acid (**DNA**, the genetic material in cells). **Ultraviolet radiation** (UVA, UVB, and UVC) from the Sun is also carcinogenic and can lead to different types of skin cancer.

arsenic: toxic element of the phosphorus group

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

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

For a substance to be declared a carcinogen there must exist sufficient evidence of a relationship between exposure to that substance and cancer in humans or animals. Because the use of human test subjects is deemed unethical, testing is done on animals (e.g., mice and rats) and on animal and human cell **cultures** (specialized nutrient-rich growth media); the data are then extrapolated to humans. An agent's potential carcinogenicity in humans is also determined from what is known of that agent's effect at the molecular level (i.e., damage to DNA/protein) or from anecdotal evidence (e.g., UV exposure and cancer).

culture: living material developed in prepared nutrient media

The potency of a carcinogen is expressed as the dose rate that, when administered chronically throughout the standard life span of a test species, will reduce the probability of the population remaining tumorless for that period by 50 percent. Called the TD50 value, the rate is measured in milligrams per kilogram [mg/kg] body weight per day. Hence, the lower the TD50 value, the more potent the carcinogen. Caution is necessary in extrapolating TD50 values from animal systems to humans, however, because the pathway through which that substance becomes carcinogenic may be absent in humans. SEE ALSO Mutagen; Teratogen.

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Careers in Chemistry

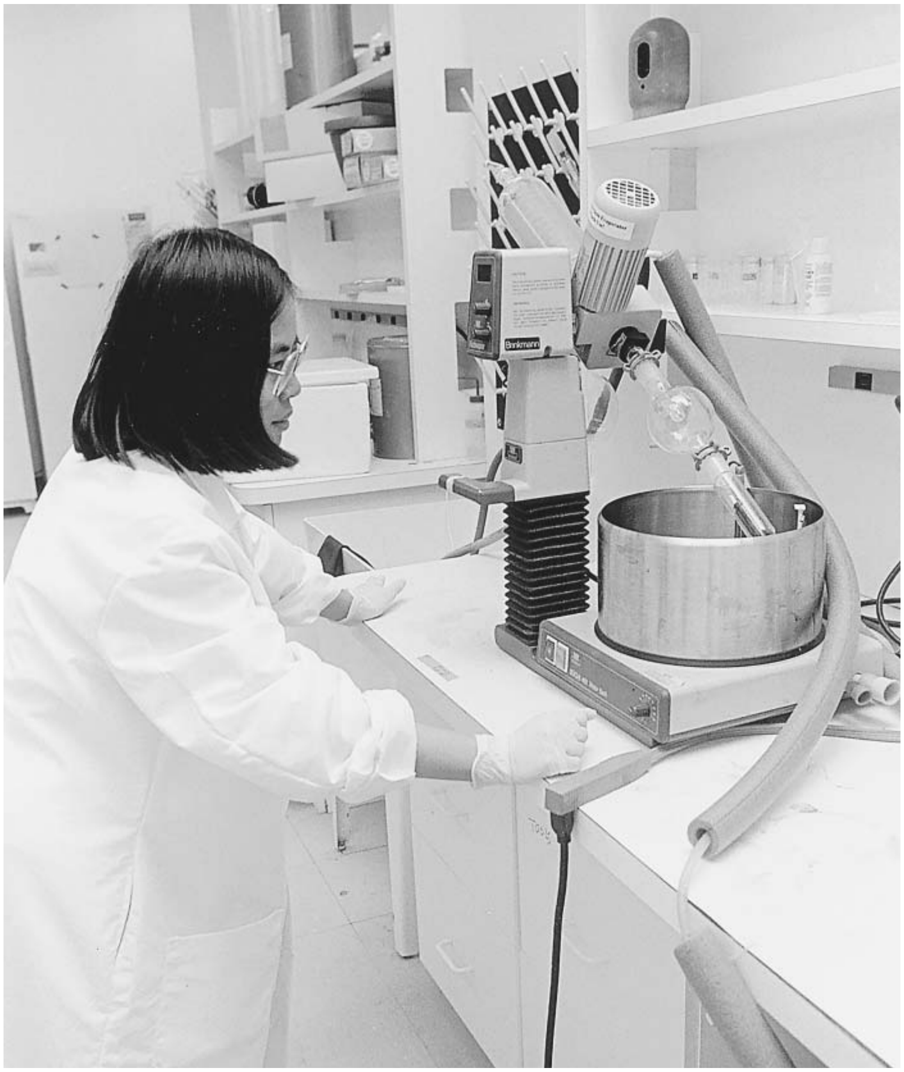
An undergraduate program in chemistry prepares the ground for many possible career paths, including industry, graduate work, and professional programs.

Choosing a college is beyond the scope of this discussion, but any U.S. school being considered for chemistry studies should offer a degree in chemistry approved by the American Chemical Society, the major professional association of chemists in the United States. Another critical criterion for college selection is the availability of undergraduate research work, a very valuable experience for a chemistry undergraduate; summer research at another college is a possible alternative, as is summer employment related to chemistry. The size of the educational institution is a matter of personal preference. Some students prefer the faculty contact that is available to them at a small liberal arts college, and others desire the wider social and academic choices that they have at a large institution.

Most colleges have a basic curriculum that gives students a broad background, but it is still possible for those students to pick courses that support future career plans. For the student leaning toward science, composition and speech courses are always valuable, as are computer courses (including courses in spreadsheet and database fundamentals, computer electronics, and computer networking). Business courses are a useful preparation for management or chemical sales positions. Most chemistry programs require several mathematics courses. Even if not required, courses in statistics, differential equations, and matrix mathematics are, for chemistry students, valuable assets. The same is true for biology and biochemistry courses.

What Does a Chemist Do in Industry?

Very often, graduates with bachelor of science degrees begin industrial careers as bench chemists, that is, individuals who work directly with chemicals under the supervision of a chemist with a Ph.D. or M.S. degree. Entry-level jobs are usually either quality control jobs (chemical analysis work) or research assistant jobs (one helps to develop new products or to improve existing products). Relatively few chemists remain at these bench jobs for their entire careers (which is why a good undergraduate program includes preparation for other job options—such as sales, customer service, or instrument development).



Many chemists begin their careers as bench chemists, in quality control, or as research assistants.

Many companies support employees who pursue further education, with partial or full payment of graduate tuition, released time (with or without pay), and even the option of doing joint research at the company (which may fulfill the graduate research requirement). When interviewing, job seekers should check on the availability of graduate programs. They should be warned that going to graduate school while working full time requires tremendous organization and motivation.

Graduate School in Chemistry and Biochemistry

A doctoral program in chemistry often lasts more than five years. Money is not usually a deciding factor, as matriculation within a chemistry graduate school usually includes an assistant teaching position that pays tuition and living costs. The Ph.D. degree is normally a research degree, and so it requires a commitment to doing research. A master's degree is all that some students will desire. It is also the way to go for students who wish to remedy academic deficiencies before doing advanced work.

Research advisers usually expect students pursuing doctorate degrees to spend at least forty to sixty hours a week on research. Graduate courses can be tremendously challenging and can require a heavy time commitment. Most graduate students doing research view college vacation time as the best time to get work done (graduate students do not have the long vacations they knew as undergraduates).

Although graduates who obtain doctorate degrees from well-known schools have an advantage when looking for employment, a great many other factors are important in a job search. Some departments or individual faculty members have relationships with particular companies (which also helps when one is looking for a position after graduation). Graduate programs in polymer chemistry, analytical chemistry, or materials sciences provide excellent job opportunities, but are often found at schools that are not highly ranked overall.

The main areas of graduate research correspond to the subject matter of typical undergraduate courses: biochemistry, analytical chemistry, inorganic chemistry, organic chemistry, and physical chemistry. One can tentatively identify areas of interest based on one's experience of these courses. One can then look for graduate schools that have advisers working in one's chosen area (or areas). Selecting a research adviser is one of the most important decisions of a career. Looking up graduate departments in the *American Chemical Society Directory of Graduate Research*, one can easily find out the research fields and publications records of faculty members. Faculty members who have published a small number of articles in refereed journals within the preceding five years may not be still active in research.

Alternative Careers

The applications of chemistry within biology are so important that many chemistry departments have become departments of chemistry and biochemistry, or departments of biological chemistry, and some offer both chemistry and biochemistry majors. Biochemistry is one of the major growth areas in chemistry. Although mergers in the pharmaceutical industry have eliminated some research laboratories, this contraction has been offset by an expansion of startup biotechnology companies.

A strong undergraduate program in chemistry or biochemistry is an excellent preparation for professional programs in medicine, optometry, chiropractic, and osteopathy. The combination of chemistry and law school is a powerful one, but one that is not often thought of. Other areas to be considered by chemistry undergraduates are food chemistry, textile and fabric chemistry, forensic science, industrial hygiene, and **toxicology**. Although the number of jobs available in these fields may be limited, there are few students who have acquired credentials in them, and so the employment opportunities can be excellent. The World Wide Web may be used to obtain more information about these fields and to locate a school with the desired program.

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

Some graduates will not want to limit their job searches to the chemical industry. The analytical thinking and organizational skills typical of successful chemistry majors make them strong candidates for positions as patent examiners or stock analysts. The combination of chemistry with computer science is attractive to many employers. Chemistry majors interested in art or writing may want to consider careers in science journalism or science illustration (although finding training and employment in these areas can be difficult).

A researcher is spraying decontamination foam in a laboratory to test the neutralization of chemical weapons.

Those who wish to teach chemistry will find opportunities at all levels, from middle school to universities. In general, the higher the level of the educational institution, the more education required. High school teachers usually start out with a secondary education degree, and then earn a master's degree while teaching. Teaching at a four-year college typically requires a Ph.D. degree. Because research is not emphasized at two-year colleges, an M.S. degree is often the appropriate certification for teaching at this level. Postdoctoral work is typically a requirement for teaching at a doctoral institution, and at some four-year colleges. SEE ALSO CHEMICAL ENGINEERING; FORENSIC CHEMISTRY; INDUSTRIAL CHEMISTRY, INORGANIC; INDUSTRIAL CHEMISTRY, ORGANIC.

Harry E. Pence

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More information available from <http://www.oneonta.edu/~pencehe/careers.html>

Carnot, Sadi

FRENCH PHYSICIST AND ENGINEER
1796–1832

Nicolas-Léonard-Sadi Carnot was born in 1796 in Paris. He is known as the father of thermodynamics. Originally a military engineer, he developed a keen interest in industry and especially the steam engine. He took a leave of absence from the military to devote more time to pursuing these interests.

Carnot published only one work in his lifetime—an essay that detailed the industrial, political, and economic importance of the steam engine. This essay also introduced the concept of the ideal steam engine and reported on the factors involved in the production of **mechanical energy** from heat. Carnot used the analogy of a waterfall to understand the ideal steam engine, positing that, as height and quantity of water determine the power of a waterfall, temperature drop and quantity of heat determine the power of a steam engine. Although his theory was not completely accurate, Carnot did make the correct observation that the power produced in a steam engine is dependent on a change in temperature.

mechanical energy: energy of an object due to its position or motion

Carnot died of cholera at a relatively young age, and this effectively ended the study of thermodynamics for almost two decades. It was not until 1850, when the English physicist William Thomson confirmed some of Carnot's theories, that his ideas on thermodynamics were more broadly applied. In fact, both the first and second laws of thermodynamics can be derived by extending Carnot's early theories. SEE ALSO THERMODYNAMICS.

Lydia S. Scratch

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Carothers, Wallace

AMERICAN CHEMIST
1896–1937

Wallace Hume Carothers, one of the founders of the modern synthetic materials industry, was born in Burlington, Iowa, on April 27, 1896. At first, his

A nylon-fiber manufacturing plant. Wallace Carothers was part of the team that first produced nylon, a material used in the manufacturing of carpeting.

education was directed not toward chemistry, but toward accounting. In 1915 he graduated from the Capital City Commercial College in Des Moines, Iowa, where his father was an instructor. He then attended Tarkio College in Missouri, where he taught accounting while studying for a bachelor's degree in science. For a brief time during World War I, he was actually the head of the chemistry department there. Carothers graduated in 1920 and went on to receive a master's degree at the University of Illinois at Urbana in 1921. After teaching for a year at the University of South Dakota, where he began serious work on organic chemistry, he returned to his studies at the University of Iowa, where he earned his doctorate in chemistry in 1924. Carothers taught for several years at Iowa and was then recruited by Harvard University. He found that he liked research better than teaching, however, and when the E. I. du Pont de Nemours & Co. asked him to direct its research in organic chemistry, he accepted the post in 1928. His principal area of interest was in polymers (long-chain molecules), particularly high molecular weight compounds, both their fundamental properties and their suitability for commercial exploitation.

Carothers's early research at Du Pont focused on products related to acetylene, whose molecules were known to form long chains. With Arnold Collins, in 1931, he produced polychlorobutadiene, better known by its commercial name Neoprene, the first wholly synthetic rubber to be manufactured commercially (beginning in 1933).

Du Pont was particularly interested in developing synthetic fibers. Because of political and trade problems resulting from Japan's war in China, the United States's main source of silk was restricted, so work was directed toward producing an artificial substitute. Carothers believed that polycondensation, in which polymers are formed by condensation and the elimination of small molecules such as water, would yield interesting new materials. His work with **dibasic acids** (acids with two hydrogen atoms, such as sulfuric acid [H_2SO_4]) and **dihydroxy compounds** (compounds with two OH- ions, such as tartaric acid [2,3-dihydrobutanedioic acid] produced different

dibasic acid: acidic substance that incorporates two acidic hydrogen atoms in one molecule, such as sulfuric (H_2SO_4) acid

dihydroxy compound: compound with molecules that incorporate two hydroxyl groups (–OH) in its structure, such as 1,2 dihydroxy ethane (sometimes called glycol) and the three dihydroxy benzene compounds kinds of polyesters, but because they had low melting points and were either water-soluble or dissolved in dry cleaning fluids, they were not commercially viable. Part of the problem with polyesters was that they were chemically related to fats and oils, and were not particularly stable.

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

Carothers turned to another group of chemicals, collectively known as polyamides. Silk, produced by the silkworm, is the best-known natural polyamide fiber. Synthetic polyamides were made by mixing dibasic acids with **diamines**. (Amines are compounds that replace one or more of the hydrogen atoms in ammonia with organic groups. Diamines contain two amino [-NH_2] groups, and are found in many important organic molecules such as glutamine [$C_5H_{10}N_2O_3$].) The products of these reactions were synthetic proteins and tended to be very stable molecules. A number of different materials with good qualities were produced, but because of the cost of their base materials, were not manufactured commercially. Then Carothers and his team attempted to use adipic acid and hexamethylenediamine (1,6-diaminohexane), which could be made from benzene, a widely available material. This produced long fibers of 6,6′-polyamide, later named Nylon 66. Patented in 1937, nylon went into commercial production in 1939 and was an immediate success. To promote the new fiber, Du Pont showed nylon stockings at the New York World's Fair that same year, advertising it as a material made from coal, air, and water. During World War II nylon production was shifted to meet wartime needs, especially for parachutes. When the war ended and Du Pont resumed commercial production, there was such a high demand for nylon stockings that fights actually broke out in stores for the limited supplies.

Carothers published over sixty scientific papers and held numerous patents, and was the first organic chemist elected to the National Academy of Sciences. Nylon was and continues to be an important product, but Carothers did not live to see its success. Throughout his life, he had suffered from bouts of severe depression. Early in 1937 his sister died suddenly and he subsequently went into a deep depression. On April 29, 1937, Carothers committed suicide, prematurely ending one of the most productive careers in chemistry. SEE ALSO NYLON; POLYMERS, SYNTHETIC.

Andrew Ede

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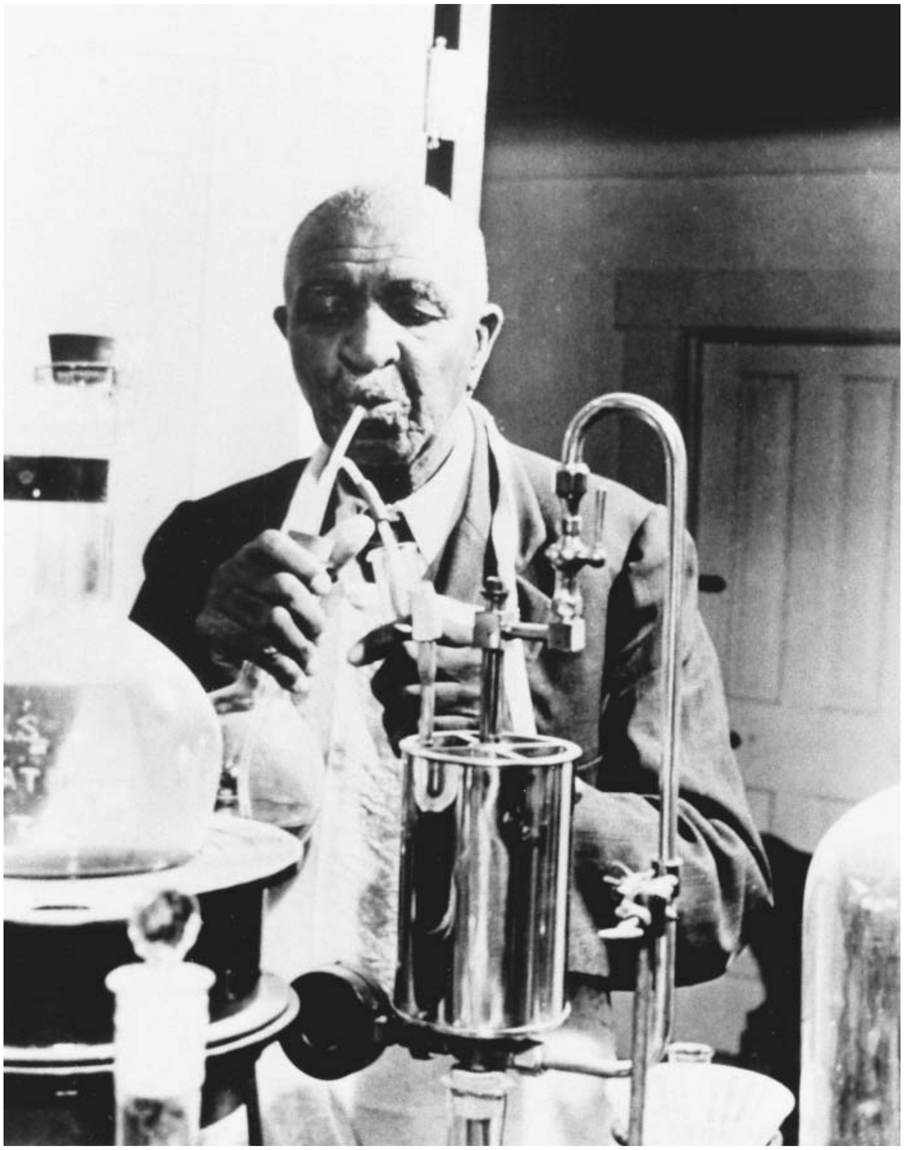
Carver, George Washington

AMERICAN BOTANIST
c. 1864–1943

George Washington Carver was born on a Missouri farm near Diamond Grove sometime toward the end of the U.S. Civil War. The exact date of



American botanist George Washington Carver was interested in industrial applications for organic raw materials. He developed hundreds of products—from shaving cream to synthetic rubber—from agricultural products.

his birth was never recorded, although later in life Carver gave the year as 1864. His father died in an accident prior to or shortly after Carver's birth. His mother Mary was kidnapped with her infant son by slave raiders shortly after his birth. Although Carver was eventually returned to Moses and Susan Carver in exchange for a horse, his mother was never heard from again.

Carver was not a strong child and this prevented him from working the fields. Instead, he helped with household chores and gardening. It is likely that these duties and the hours spent exploring the woods surrounding his home induced his keen interest in plants and led to his life of study and scholarly pursuits. He gathered and cared for a wide variety of plants from throughout the region and frequently helped friends and neighbors treat ailing plants.

As an adolescent, Carver was sent to Neosho, Missouri, where he worked as a farmhand and studied in a one-room schoolhouse. From there, he moved to Kansas and attended Minneapolis High School. In 1885, as a young adult, Carver was accepted to Highland University in Kansas on scholarship. However, when he showed up the first day of class, the president of the university is said to have denied him entrance because of his race. Other colleges rejected him for the same reason, but that did not stop Carver from attempting to seek a higher education.

In 1890 Carver entered Simpson College, a Methodist school in Indianola, Iowa, to study piano and art. While he excelled at both, his art instructor Etta Budd recognized his horticultural talent. She persuaded him to pursue a more pragmatic career in scientific agriculture. In 1891 Carver transferred to the Iowa State College of Agriculture and Mechanic Arts, which is now Iowa State University. Carver was the first African-American student accepted by the college.

As an undergraduate student, Carver was a leader. He became involved in all facets of university life; his poetry was published in the student newspaper and his paintings exhibited at the 1893 World's Fair in Chicago. It was for his excellence as a botanist, however, that he earned his B.S. in agriculture in 1894. Joseph Budd (Etta's father and a professor of horticulture) and Louis Pammel (a botany professor) encouraged Carver to stay on as a graduate student. His proficiency in plant breeding soon led to his appointment as a member of the Iowa State faculty. Over the next two years, Carver's extensive work in plant pathology and mycology (the branch of botany that studies fungi) prompted him to publish several articles, and, as a consequence, he gained national respect as a scientist. In 1896 he earned his M.S. in agriculture from Iowa State and was invited by Booker T. Washington to join Alabama's Tuskegee Institute.

At Tuskegee, Carver found his intellectual home. As the director of its Agricultural Experiment Station, he was given a barren 21-acre plot to work on. Carver and his students conducted experiments on crops requiring low input and capable of fixing nitrogen, such as the cowpea and the peanut. The resulting soil enrichment substantially increased crop production and became an accepted agricultural practice for both cotton and tobacco growers.

It was working with the surplus of peanuts that this practice produced that led to Carver's reputation as a "chemurgist," a chemist interested in the industrial applications of organic raw materials and particularly farm products. His research resulted in the creation of over 325 different products from peanuts, ranging from buttermilk to shaving cream to synthetic rubber. He generated 108 products from the sweet potato and invented countless other products from a wide variety of agricultural plants—everything from pecans to soybeans. Indeed, Carver pursued **biomass** conversion with a zeal that is only now being matched as contemporary society searches for alternatives to fossil fuel consumption.

biomass: collection of living matter

Toward the end of his life, Carver received numerous accolades and honors; a feature film about his life was even produced in 1938. He died on January 5, 1943. In 1994 Iowa State posthumously awarded Carver the degree of Doctor of Humane Letters. This was a fitting tribute to a life spent in the pursuit of knowledge. SEE ALSO AGRICULTURAL CHEMISTRY.

Todd W. Whitcombe

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Catalysis and Catalysts

Catalysis is an acceleration or **retardation** of the rate of a chemical reaction, brought about by the addition of a substance (the **catalyst**) to the reaction medium. The catalyst, usually present in small amounts, is not consumed in the reaction. Catalysis today is almost always associated with rate acceleration, and is very important in industry because rate acceleration usually means that a chemical compound can be made more cheaply and cleanly. It is hard to envision what modern society would be like without its use of myriad chemicals, polymers, and pharmaceuticals, most of which are prepared industrially by catalytic chemistry.

retardation: to slow down a chemical reaction

catalyst: substance that aids in a reaction while retaining its own chemical identity

The rate of reaction refers to the amount of reactant consumed or product formed per unit of time at a given temperature and pressure. Generally speaking, the rate of reaction goes up as the temperature of the reaction is raised. This is related to the fact that most reactants have to "climb" over one or more energy barriers to reach the product stage. This can be likened to one's climbing a hill. The taller the hill, the more energy one expends in reaching its top. Reactants must become energetic enough to "reach" the top of an energy barrier if a reaction is to occur. Raising the reaction temperature ultimately imparts more energy to the reactants, creating a greater probability that more of them will be energetic enough to traverse the barrier, and this results in a faster rate.

What does a catalyst do? First of all, a catalyst does not change the energetic characteristics of the reactants and products and the barriers between them. It instead finds an alternate reaction pathway that bridges reactants and products, and one that has lower (and thus easier-to-traverse) energy barriers. An alternate pathway means a faster reaction rate. Although a catalyst can itself be considered a reactant, it is regenerated, unchanged, at a later stage in the catalytic process. The regenerated catalyst can then be used to catalyze another like reaction. Thus, in principle, only a very small amount of catalyst is needed to generate copious amounts of product. This is desirable, as many catalysts that are used industrially are very expensive.

Homogeneous catalysis refers to catalytic reactions in which the catalyst is in the same **phase** as the reactant. This is most often the liquid phase, although gas phase examples are known. Ozone in the **stratosphere**, for example, is converted into oxygen via the catalytic action of chlorine atoms formed as a result of the photochemical destruction of **chlorofluorocarbon** refrigerants.

The Fischer **esterification**, named after the eminent German chemist Emil Fischer, is the Brønsted acid–catalyzed reaction of an alcohol with a **carboxylic acid** to form an **ester** (see Table 1). Sulfuric acid is often the catalyst. Esters are widely used in the soap, perfume, and food industries.

homogeneous: relating to a uniform mixture of substances

phase: homogeneous state of matter consisting of gases, liquids, or solids

stratosphere: layer of the atmosphere where ozone is found; starts about 10 km (6.2 mi) above ground

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

esterification: chemical reaction in which esters (RCO_2R') are formed from alcohols (R_1OH) and carboxylic acids (RCO_2H)

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

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; a compound with the general formula RC(O)OR′

EXAMPLES OF CATALYTIC REACTIONS

Type	Reaction Phase(s)	Reaction	Catalyst	Name of Process/Reaction
homogeneous	gas	ozone → oxygen	chlorine atom	ozone depletion
	liquid	alcohol + acid → ester	sulfuric acid	Fischer esterification
	liquid	arene + acid chloride → ketone	aluminum chloride	Friedel-Crafts acylation
	liquid	methanol + CO → acetic acid	rhodium salts $+1^-$	Monsanto process
heterogeneous	gas-solid	$3H_2 + N_2 \rightarrow 2NH_3$	iron	Haber process
	gas-liquid-solid	alkene + H_2 → alkane	transition metals such at Pt and Pd	catalytic hydrogenation
	gas-solid	crude oil → gasoline	zeolite	catalytic cracking
	liquid-solid	waste water + H_2O_2 (O_2) → clean water	titanium dioxide	photocatalysis
enzyme	water	starch → D-glucose	α-Glucosidase	hydrolysis
	water	cellulose → D-glucose	β-Glucosidase	hydrolysis

Table 1. Examples of catalytic reactions.

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 RFC(O)R functional group

The Friedel–Crafts acylation reaction, named after the French and American chemists who discovered it, used to prepare aryl **ketones**, is catalyzed by the Lewis acid aluminum chloride. Although aluminum chloride is a catalyst, it must be used (in Friedel–Crafts reactions) in stoichiometric amounts, as the portion of aluminum chloride that is catalytically inactive strongly binds to the product. Because aluminum chloride is corrosive and difficult to handle and must be destroyed when the reaction is complete, chemists continue to seek more environmentally friendly catalysts for this reaction.

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

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

Transition metal salts and complexes also serve as homogeneous catalysts. In the Monsanto process, rhodium salts plus iodide convert methanol and carbon monoxide into an industrially useful carboxylic acid, acetic acid. The rhodium **metal** serves as the primary reaction site; it binds the reactants and subsequently unbinds the products. The key reactions at the metal reaction site are called oxidative addition and reductive elimination.

Heterogeneous catalysis describes reactions in which the catalyst and the reactants are in different phases. In these reactions the catalyst is most often an insoluble solid and the reactants are in the gaseous or liquid/solution phase. A key feature of this type of catalysis is that the reactants must adsorb to the catalyst's surface. Large catalyst surfaces, then, ensure that the desired reaction occurs rapidly.

feedstock: mixture of raw materials necessary to carry out chemical reactions

synthesis: combination of starting materials to form a desired product

In the Haber process, named after its German discoverer, gaseous hydrogen and nitrogen are converted into ammonia over an iron catalyst under pressure and elevated temperature. Ammonia is a **feedstock** for the **synthesis** of fertilizers, explosives, and dyes. L-dopa, a drug used in the treatment of Parkinson's disease, is prepared via a hydrogenation reaction (the addition of hydrogen) over a solid transition metal catalyst. Margarine is, likewise, synthesized via a hydrogenation reaction.

Crude oil is converted into gasoline in cracking reactions that transform large molecules into smaller ones. The catalytic reactions occur in the interiors of porous inorganic solids called zeolites. The actual catalysts are protons that exist on the interior walls of the zeolites. Titanium dioxide, a photocatalyst, is an interesting solid because it functions as a catalyst only when it is exposed to light. This is environmentally advantageous, as the combination of titanium dioxide and light can be used to catalyze the removal of pollutants from water via their oxidization with hydrogen peroxide or oxygen.

Most useful compounds require more than one reaction for their syntheses, all of which may be catalytic. A good illustration of this is the three-step synthesis of the **analgesic** agent ibuprofen. The first reaction of the synthesis of ibuprofen is a homogeneous, hydrogen fluoride–catalyzed, Friedel–Crafts acylation reaction; the second, a heterogeneous, palladium-catalyzed, hydrogenation reaction; and the third, a homogeneous, palladium-catalyzed, carbonylation reaction (addition of carbon monoxide).

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

Enzyme catalysis, a form of homogeneous catalysis, refers to the catalytic chemistry that controls the rates of virtually all reactions occurring in living systems. Enzymes, which serve as biological catalysts, are high molecular weight polymers made up from twenty different monomers called amino acids. The linked amino acids have a common backbone, but differing side chains of great structural and chemical variety, and an overall confirmation of great complexity.

An enzyme, in general, functions by first binding the reactant to a site on its surface called the active site. It is here that the catalytic chemistry occurs. The bound reactant then interacts and reacts with the side chains of the amino acids that make up the enzyme, and it is this interaction that brings about the chemical transformation. When the reaction is complete, the bound product diffuses away from the active site. Enzyme reactions take place in water, the biological solvent, at ambient temperatures. They often occur at rates a million or more times faster than those of uncatalyzed reactions. Hundreds of thousands of reactions can occur at the site of a single enzyme in one second. Many enzymes require the assistance of a molecule called a coenzyme if the catalytic reaction is to occur. Other enzymes require **metal cations**, such as Zn^{+2}, at their active sites.

metal cation: positively charged ion resulting from the loss of one or more valence electrons

When we eat, our mouths very often experience a sweet taste. This sweetness is due to the conversion of starch polymer molecules into the sugar D-glucose by the enzyme α-glucosidase, present in saliva. The polymer cellulose, structurally related to starch, is converted into D-glucose by the enzyme β-glucosidase (but only in bacteria). There are enzymes in the stomach and gut that aid digestion. The liver produces enzymes that are instrumental in removing toxic compounds from blood. Yeast organisms contain enzymes that convert sugar into ethanol and carbon dioxide—important in the making of bread and alcoholic beverages. Even the genetic material **DNA** (and its ancillary material **RNA**) is made by and functions by participation in enzyme-catalyzed reactions. Interestingly, DNA and RNA are also instrumental in synthesizing these very same enzymes. SEE ALSO KINETICS; REACTION RATES.

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

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

Richard Pagni

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Cavendish, Henry

ENGLISH PHYSICIST AND CHEMIST
1731–1810

Henry Cavendish, born in Nice, France to an aristocratic English family, was an avid and excellent experimenter. At the age of forty, he inherited an immense fortune that afforded him the luxury of pursuing his scientific interests (he was described by some as the "richest of all the learned and the most learned of all the rich"). He was an extraordinarily odd man, whose extreme shyness rendered him a virtual recluse. Despite this, he is remembered as a great, albeit humble, man who devoted his life to science.

English chemist and physicist Henry Cavendish, who discovered hydrogen.

Cavendish explored all areas of science, including astronomy, optics, electricity, geology, and pure mathematics. Among his accomplishments are the first calculation of Earth's mass (his results were just 10% off modern measurements) and the introduction of the concept of **voltage**. His principal interest nevertheless was experimental chemistry. His most famous contribution to science was the discovery and description of the properties of hydrogen and its status as a constituent element in water.

voltage: potential difference expressed in volts

Cavendish, like many before him, noticed that a gas was produced when zinc or iron was dropped into an acid. He called this gas "inflammable air" (known today as hydrogen). Using his exacting experimental skills, Cavendish was the first to distinguish this inflammable air from ordinary air and to investigate its specific properties. He presented a paper detailing his findings in 1766.

The importance of inflammable air became clear about fifteen years after Cavendish presented his paper. Joseph Priestley (1733–1804) was also interested in gases, and in 1781 told Cavendish of the results of some of his own experiments. When Priestley used an electrostatic machine to spark ordinary air with inflammable air, he noticed that water was formed. Cavendish repeated this experiment, as well as others like it, but using oxygen (or, as he called it, "dephlogisticated air") in place of ordinary air.

Cavendish's results were the same as Priestley's, but he did not publish or present his findings. Sometime before 1783, however, Cavendish did advise Priestley of his results. Priestley told Charles Blagden, secretary of the **Royal Society** in London, and Blagden in turn informed Antoine Lavoisier (1743–1794) in France.

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

Cavendish did eventually publish his findings on the formation of water in 1784. But Lavoisier claimed that *he* had discovered how water was formed—in fact, it was Lavoisier who coined the name "hydrogen," which means "water former." It was not until the mid-nineteenth century, when Cavendish's notebooks were published, that he was given sole credit for discovering that water is composed of inflammable air and dephlogisticated air, or hydrogen and oxygen.

As may be seen in his collaborative work with Priestley in the investigation of the composition of water, Cavendish did not allow his natural shyness to impede his work. The relationship between him and Priestley demonstrates not only Cavendish's devotion to science, but the general cooperative nature of scientific investigation. By sharing the results of their separate experiments, these two great scientists were able to discover the composition of water.

For all of his scientific genius, Cavendish was a pronounced eccentric. He rarely left his house except for weekly meetings of the Royal Society, and even there, despite being one of the most famous scientists of his time, he was known to linger outside the meeting room and enter only when he thought no one would notice. He could barely tolerate the company of women; if any of his female servants happened to cross his path, she was likely to be fired. Though enormously wealthy, he was reputed to own but one suit, and an old-fashioned one at that.

Cavendish lived a lonely and humble life, committed to the cultivation of science. To him, science was measurement, and he showed himself to be one of the most respected experimentalists of the time. His death was as lonely as his life; when he sensed that the end was near, he instructed his servant to leave the room and not come back until a certain time. When the servant returned, he found that Cavendish had died. SEE ALSO HYDROGEN; LAVOISIER, ANTOINE; PRIESTLEY, JOSEPH.

Lydia S. Scratch

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Cellulose

Cellulose is the most abundant organic molecule in nature. It is a polysaccharide assembled from **glucose** monomer units, and it (together with other materials such as hemicellulose and lignin) is the main constituent of plant cell walls. Along with several undigestible polysaccharides, cellulose constitutes the main part of dietary fiber. Specifically cellulose is one of the components of insoluble fiber.

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

The glucose units in cellulose are combined in a way that results in the formation of very linear, flat molecules that can, in turn, form sheets that possess extensive networks of **hydrogen bonds**. The hydrogen bonds are both within individual sheets and between successive sheets. As a result of these bonds, sheets of cellulose are particularly strong—a property critical to the function of plant cell walls. Cellulose shows a variable degree of polymerization, with anywhere from 1,000 to 14,000 glucose residues comprising a single cellulose polymer. Because of its high molecular weight and crystalline structure, cellulose is insoluble in water and has a poor ability to absorb water.

hydrogen bond: interaction between H atoms and lone pair electrons that constitutes hydrogen bonding

Human beings lack the enzyme cellulase and are therefore unable to break cellulose down to individual glucose molecules. Although many fungi are able to break down cellulose to glucose, only a few types of bacteria have

rumina: multiple stomachs found in grass-eating animals; digestion of cellulose is carried out in these stomachs

this ability. In the **rumina** of cows, sheep, and goats, two different types of bacteria produce the enzyme that breaks down cellulose.

Cellulose and its derivatives are used in a number of food products to modify those foods in different ways (e.g., as a thickener, stabilizer, or texturizer). The fibrous form is a basic material that is used to make both textiles and paper. Cellulose is also used to make nitrocellulose (an ingredient in explosives and lacquers) and as a binder in the manufacture of medicinal tablets. SEE ALSO Fibers; Polymers, Natural; Polysaccharides.

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Ceramics

Ceramics can be defined as heat-resistant, nonmetallic, inorganic solids that are (generally) made up of compounds formed from metallic and nonmetallic elements. Although different types of ceramics can have very different properties, in general ceramics are corrosion-resistant and hard, but brittle. Most ceramics are also good insulators and can withstand high temperatures. These properties have led to their use in virtually every aspect of modern life.

The two main categories of ceramics are traditional and advanced. Traditional ceramics include objects made of clay and cements that have been hardened by heating at high temperatures. Traditional ceramics are used in dishes, crockery, flowerpots, and roof and wall tiles. Advanced ceramics include carbides, such as silicon carbide, SiC; oxides, such as aluminum oxide, Al_2O_3; nitrides, such as silicon nitride, Si_3N_4; and many other materials, including the mixed oxide ceramics that can act as superconductors. Advanced ceramics require modern processing techniques, and the development of these techniques has led to advances in medicine and engineering.

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

Glass is sometimes considered a type of ceramic. However, glasses and ceramics differ in that ceramics have a crystalline structure while glasses contain impurities that prevent **crystallization**. The structure of glasses is amorphous, like that of liquids. Ceramics tend to have high, well-defined melting points, while glasses tend to soften over a range of temperatures before becoming liquids. In addition, most ceramics are opaque to visible light, and glasses tend to be translucent. Glass ceramics have a structure that consists of many tiny crystalline regions within a noncrystalline matrix. This structure gives them some properties of ceramics and some of glasses. In general, glass ceramics expand less when heated than most glasses, making them useful in windows, for wood stoves, or as radiant glass-ceramic cooktop surfaces.

Composition

Some ceramics are composed of only two elements. For example, alumina is aluminum oxide, Al_2O_3; zirconia is zirconium oxide, ZrO_2; and quartz is

Ceramics are good insulators and can withstand high temperatures. A popular use of ceramics is in artwork.

silicon dioxide, SiO_2. Other ceramic materials, including many minerals, have complex and even variable compositions. For example, the ceramic mineral feldspar, one of the components of granite, has the formula $KAlSi_3O_8$.

The chemical bonds in ceramics can be covalent, ionic, or polar covalent, depending on the chemical composition of the ceramic. When the components of the ceramic are a **metal** and a nonmetal, the bonding is primarily ionic; examples are magnesium oxide (magnesia), MgO, and barium titanate, $BaTiO_3$. In ceramics composed of a **metalloid** and a nonmetal, bonding is primarily covalent; examples are boron nitride, BN, and silicon carbide, SiC. Most ceramics have a highly crystalline structure, in which a three-dimensional unit, called a unit cell, is repeated throughout the material. For example, magnesium oxide crystallizes in the rock salt structure. In this structure, Mg^{2+} ions alternate with O^{2-} ions along each **perpendicular** axis.

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

metalloid: element that exhibits properties that are between those of metals and nonmetals; generally considered to include boron, silicon, germanium, arsensic, antimony, tellurium, and polonium

perpendicular: condition in which two lines (or linear entities like chemical bonds) intersect at a 90-degree angle

Manufacture of Traditional Ceramics

Traditional ceramics are made from natural materials such as clay that have been hardened by heating at high temperatures (driving out water and allowing strong chemical bonds to form between the flakes of clay). In fact, the word "ceramic" comes from the Greek *keramos*, whose original meaning was "burnt earth." When artists make ceramic works of art, they first mold clay, often mixed with other raw materials, into the desired shape. Special ovens called kilns are used to "fire" (heat) the shaped object until it hardens.

Clay consists of a large number of very tiny flat plates, stacked together but separated by thin layers of water. The water allows the plates to cling together, but also acts as a lubricant, allowing the plates to slide past one another. As a result, clay is easily molded into shapes. High temperatures drive out water and allow bonds to form between plates, holding them in place and promoting the formation of a hard solid. Binders such as bone ash are sometimes added to the clay to promote strong bond formation, which makes the ceramic resistant to breakage. The common clay used to make flowerpots and roof tiles is usually red-orange because of the presence of iron oxides. White ceramics are made from rarer (and thus more expensive) white clays, primarily kaolin.

The oldest known ceramics made by humans are figurines found in the former Czechoslovakia that are thought to date from around 27,000 B.C.E. It was determined that the figurines were made by mixing clay with bone, animal fat, earth, and bone ash (the ash that results when animal bones are heated to a high temperature), molding the mixture into a desired shape, and heating it in a domed pit. The manufacture of functional objects such as pots, dishes, and storage vessels, was developed in ancient Greece and Egypt during the period 9000 to 6000 B.C.E.

An important advance was the development of white porcelain. Porcelain is a hard, tough ceramic that is less brittle than the ceramics that preceded it. Its strength allows it to be fashioned into beautiful vessels with walls so thin they can even be translucent. It is made from kaolin mixed with china stone, and the mixture is heated to a very high temperature (1,300°C, or 2,372°F). Porcelain was developed in China around C.E. 600 during the T'ang dynasty and was perfected during the Ming dynasty, famous for its blue and white porcelain. The porcelain process was introduced to the Arab world in the ninth century; later Arabs brought porcelain to Spain, from where the process spread throughout Europe.

Bone china has a composition similar to that of porcelain, but at least 50 percent of the material is finely powdered bone ash. Like porcelain, bone china is strong and can be formed into dishes with very thin, translucent walls. Stoneware is a dense, hard, gray or tan ceramic that is less expensive than bone china and porcelain, but it is not as strong. As a result, stoneware dishes are usually thicker and heavier than bone china or porcelain dishes.

Manufacture of Advanced Ceramics

The preparation of an advanced ceramic material usually begins with a finely divided powder that is mixed with an organic binder to help the powder consolidate, so that it can be molded into the desired shape. Before it is fired, the ceramic body is called "green." The green body is first heated at a low temperature in order to decompose or oxidize the binder. It is then heated to a high temperature until it is "sintered," or hardened, into a dense, strong ceramic. At this time, individual particles of the original powder fuse together as chemical bonds form between them. During sintering the ceramic may shrink by as much as 10 to 40 percent. Because shrinkage is not uniform, additional machining of the ceramic may be required in order to obtain a precise shape.

Sol-gel technology allows better mixing of the ceramic components at the molecular level, and hence yields more **homogeneous** ceramics, because the ions are mixed while in solution. In the sol-gel process, a solution of an **organometallic compound** is hydrolyzed to produce a "sol," a colloidal suspension of a solid in a liquid. Typically the solution is a metal alkoxide such as tetramethoxysilane in an alcohol solvent. The sol forms when the individual formula units polymerize (link together to form chains and net-

homogeneous: relating to a uniform mixture of substances

organometallic compound: compound containing both a metal (transition) and one or more organic moieties works). The sol can then be spread into a thin film, precipitated into tiny uniform spheres called microspheres, or further processed to form a gel inside a mold that will yield a final ceramic object in the desired shape. The many crosslinks between the formula units result in a ceramic that is less brittle than typical ceramics.

Although the sol-gel process is very expensive, it has many advantages, including low temperature requirements; the ceramist's ability to control porosity and to form films, spheres, and other structures that are difficult to form in molds; and the attainment of specialized ceramic compositions and high product purity.

Porous ceramics are made by the sol-gel process. These ceramics have spongelike structures, with many porelike lacunae, or openings, that can make up from 25 to 70 percent of the volume. The pore size can be large, or as small as 50 nanometers (2×10^{-6} inches) in diameter. Because of the large number of pores, porous ceramics have enormous surface areas (up to 500 square meters, or 5,382 square feet, per gram of ceramic), and so can make excellent catalysts. For example, zirconium oxide is a ceramic oxygen sensor that monitors the air-to-fuel ratio in the exhaust systems of automobiles.

Aerogels are solid foams prepared by removing the liquid from the gel during a sol-gel process at high temperatures and low pressures. Because aerogels are good insulators, have very low densities, and do not melt at high temperatures, they are attractive for use in spacecraft.

Properties and Uses

For centuries ceramics were used by those who had little knowledge of their structure. Today, understanding of the structure and properties of ceramics is making it possible to design and engineer new kinds of ceramics.

Most ceramics are hard, chemically **inert**, refractory (can withstand very high heat without deformation), and poor conductors of heat and electricity. Ceramics also have low densities. These properties make ceramics attractive for many applications. Ceramics are used as refractories in furnaces and as durable building materials (in the form of bricks, tiles, cinder blocks, and other hard, strong solids). They are also used as common electrical and thermal insulators in the manufacture of spark plugs, telephone poles, electronic devices, and the nose cones of spacecraft. However, ceramics also tend to be brittle. A major difficulty with the use of ceramics is their tendency to acquire tiny cracks that slowly become larger until the material falls apart. To prevent ceramic materials from cracking, they are often applied as coatings on inexpensive materials that are resistant to cracks. For example, engine parts are sometimes coated with ceramics to reduce heat transfer.

inert: incapable of reacting with another substance

Composite materials that contain ceramic fibers embedded in polymer matrices possess many of the properties of ceramics; these materials have low densities and are resistant to corrosion, yet are tough and flexible rather than brittle. They are used in tennis rackets, bicycles, and automobiles. Ceramic composites may also be made from two distinct ceramic materials that exist as two separate ceramic phases in the composite material. Cracks generated in one phase will not be transferred to the other. As a result, the resistance of the composite material to cracking is considerable. Composite ceramics made from diborides and/or carbides of zirconium and hafnium mixed with silicon carbide are used to create the nose cones of spacecraft. Break-resistant cookware (with outstanding thermal shock resistance) is also made from ceramic composites.

Although most ceramics are thermal and electrical insulators, some, such as cubic boron nitride, are good conductors of heat, and others, such as rhenium oxide, conduct electricity as well as metals. Indium tin oxide is a transparent ceramic that conducts electricity and is used to make liquid crystal calculator displays. Some ceramics are semiconductors, with conductivities that become enhanced as the temperature increases. For example, silicon carbide, SiC, is used as a semiconductor material in high temperature applications.

High temperature superconductors are ceramic materials consisting of complex ionic oxides that become superconducting when cooled by liquid nitrogen. That is, they lose all resistance to electrical current. One example is the material $YBa_2Cu_3O_{7-x}$, which crystallizes to form "sheets" of copper and oxygen atoms that can carry electrical current in the planes of the sheets.

Some ceramics, such as barium ferrite or nickel zinc ferrites, are magnetic materials that provide stronger magnetic fields, weigh less, and cost less than metal magnets. They are made by heating powdered ferrite in a magnetic field under high pressure until it hardens. Ceramic magnets are brittle, but are often used in computers and microwave devices.

voltage: potential difference expressed in volts

The properties of piezoelectric ceramics are modified when **voltage** is applied to them, making them useful as sensors and buzzers. For example, lead zirconium titanate is a piezoelectric ceramic used to provide "muscle action" in robot limbs in response to electrical signals.

Some ceramics are transparent to light of specific frequencies. These optical ceramics are used as windows for infrared and ultraviolet sensors and in radar installations. However, optical ceramics are not as widely used as glass materials in applications in which visible light must be transmitted. An electro-optic ceramic such as lead lanthanum zirconate titanate is a material whose ability to transmit light is altered by an applied voltage. These electro-optic materials are used in color filters and protective goggles, as well as in memory-storage devices.

Still other ceramics are important in medicine. For example, they are used to fabricate artificial bones and to crown damaged teeth. The fact that many ceramics can be easily sterilized and are chemically inert makes ceramic microspheres made of these materials useful as biosensors. Drugs and other chemicals can be carried within microsphere pores to desired sites in the body. SEE ALSO GLASS; MINERALS; SEMICONDUCTORS; SUPERCONDUCTORS.

Loretta L. Jones

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Cerium

MELTING POINT: 798°C
BOILING POINT: 3,257°C
DENSITY: 6.773 g/cm^3
MOST COMMON IONS: Ce^{3+}, Ce^{4+}

58
Ce
CERIUM
140.12

In 1751 the Swedish chemist Axel F. Cronstedt found, near Bastnäs, Sweden, a mineral that was eventually named cerita (its name related to the planetoid Ceres). Independently, Martin Klaproth, Jöns J. Berzelius, and Wilhelm Hisinger, working with cerita, each isolated a product, ceria (in 1803), from which Carl G. Mosander obtained three different substances, as oxides: cerium, lanthanum, and a mixture of oxides known as didymia.

Cerium is the most abundant member of the **lanthanide**, or rare earth, elements. It has two stable **valence** states, Ce^{3+} (cerous) and Ce^{4+} (ceric). It is found as a **trace element** in several minerals, but only two, bastnasite, $LnFCO_3$, and monazite, $(Ln, Th)PO_4$ (where Ln = a lanthanide element, such as lanthanum, praseodymium, neodymium, or cerium), which are approximately 30 percent and 22 to 25 percent cerium, respectively, are the principal sources of this element.

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

valence: combining capacity

trace element: element occurring only in a minute amount

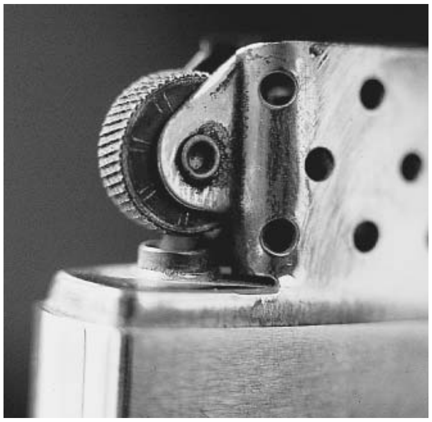
metal: element or other substance the solid phase of which is characterized by high thermal and electrical conductivities

To obtain cerium, a bastnasite concentrate is treated with sulfuric acid or hydrochloric acid, yielding the hydrated sulfate or the chloride of cerium. The sulfate is converted to the hydroxide or the carbonate, and then to the fluoride. A monozite concentrate is digested in an autoclave with an excess of caustic soda at 150°C (302°F).

$$LnTh(PO_4) + 3NaOH \rightarrow Na_3PO_4 + Ln(OH)_3 + Th(OH)_4$$

$Ln(OH)_3$ can be converted to the corresponding hydrated chloride or fluoride by treatment with the appropriate acids. These halide compounds are carefully dehydrated to yield the lanthanide anhydrous salts. Misch **metal** is a mixture of lanthanide elements (it is approximately 50% cerium), and is obtained via the electrolysis of the fused mixed lanthanide chlorides.

Of Ce(III) compounds: the nitrate, chloride, and bromide are water-soluble; the carbonate, fluoride, hydroxide, oxalate, and phosphate are water-insoluble; the acetate and sulfate are sparingly soluble. These compounds are usually prepared from a reactive precursor such as carbonate, basic carbonate, or oxide using the appropriate acids. They are practically colorless.



A cigarette lighter with a flint, which is made from cerium.

anion: negatively charged chemical unit, like Cl^{-}, CO_{32}^{-}, or NO_3^{-}

Ce(IV) compounds include soluble salts that are orange or red in color. Ceric sulfate crystals are orange, as are some complexes in which Ce(IV) is present in the **anion**. Diammonium hexanitrocerate $(NH_4)_2[Ce(NO_3)_6]$, for example, is strongly red.

There are practically no medical applications for cerium. Several metallurgical, glass, ceramic, and others applications exist, including:

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

catalysis: reaction induced by a substance that retains its own chemical identity

- lighter flints (misch metal)
- glass polishing (CeO_2 powders)
- glass decolorization (the **oxidation** of Fe^{2+} to Fe^{3+} by Ce^{4+})
- UV absorption (Ce^{4+} is opaque to near ultraviolet)
- enamels (CeO_2)
- luminescent applications
- **catalytic** (cracking crude oil to gasoline)
- vehicle emission control (CeO_2)

SEE ALSO Berzelius, Jöns Jakob; Dysprosium; Erbium; Europium; Gadolinium; Holmium; Lanthanum; Lutetium; Neodymium; Praseodymium; Promethium; Samarium; Terbium; Ytterbium.

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55
Cs
CESIUM
132.9054

Cesium

MELTING POINT: 28.5°C
BOILING POINT: 671°C
DENSITY: 1.873 g/cm^3
MOST COMMON IONS: Cs^{+}

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

fractional distillation: separation of liquid mixtures by collecting separately the distillates at certain temperatures

Cesium is an alkali **metal** that reacts explosively with water and melts just above room temperature. The word "cesium" is derived from *caesium* (Latin for "sky blue"). The name was chosen because of the blue lines observed by Robert Bunsen and Gustav Kirchhoff during their analysis of springwater with a spectroscope in 1860. Currently, cesium metal is generated via thermal decomposition of the azide, electrolysis of molten CsCN, or reduction of molten CsCl with calcium vapor followed by **fractional distillation**.

Like the other alkali metals, cesium is a soft, silvery metal, but it appears golden if it has been exposed to small amounts of oxygen. It is not found in its metallic state in nature; it is obtained as a byproduct of lithium processing of the mineral lepidolite. Its most significant ore is pollucite, and the world's largest pollucite deposit is found in Bernic Lake, Manitoba, Canada. Cesium's average crustal abundance is about 3 parts per million. Cesium is the most electropositive stable element and will ignite if exposed to air. Cesium burns blue in the flame test.

Both cesium and its compounds find practical uses. Cesium metal can be used as a getter to remove oxygen in phototubes. It is used in atomic clocks that are accurate to within five seconds per every three hundred years. (A second is defined as 9,192,631,770 oscillations of a Cs-133 atom.) CsI and CsF are used in scintillation counters to monitor ionizing radiation. CsCl is used to create density gradients for the separation and purification of **DNA** via ultracentrifugation. SEE ALSO Alkali Metals; Bunsen, Robert.

Nathan J. Barrows

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

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Chadwick, James

ENGLISH PHYSICIST
1891–1974

English physicist, Sir James Chadwick, recipient of the 1935 Nobel Prize in physics, "for the discovery of the neutron."

Sir James Chadwick was born of humble origins on October 20, 1891, to John Joseph and Anne Mary Chadwick in Clarke Lane just outside of Bollington, England. Primarily raised by his grandparents, he won a scholarship to nearby Victoria University in Manchester, where he entered the physics program by mistake. He had intended to enroll in the mathematics program, but waited in the wrong registration area so ended up being admitted to the physics department instead. Chadwick graduated in 1911 and then went to work in Ernest Rutherford's laboratory, beginning a long, productive relationship between the two men. Chadwick earned his M.S. in 1913; by the age of twenty-one he had already published five scientific papers. At that point, he won an 1851 Exhibition scholarship to study abroad for two years, whereupon he traveled to Germany to work with Hans Geiger.

During his period of study in Germany, Chadwick discovered that β-rays (electrons) are emitted in a continuous spectrum, at odds with other groups' results, and a finding that eventually led to the theory and discovery of the neutrino. While he was in Germany, World War I broke out, and Chadwick was rounded up with other English in the country and interned at Ruhleben.

After his release from Ruhleben in 1919, Chadwick followed Rutherford to the Cavendish Laboratory at Cambridge University, where he was named assistant director of research in 1923. Rutherford had been working on the disintegration of nitrogen nuclei under bombardment by **α-particles**, and Chadwick's first research upon his return to England involved the disintegration of different nuclei.

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

It was in the investigation of beryllium disintegration in 1932 that the neutron was discovered. Since the neutron has no charge, the typical electromagnetic methods of detection were useless. Chadwick bounced the mystery particle off atomic nuclei that were detectable, and, by the conservation of momentum and energy, he was able to determine that the neutron had a mass slightly greater than that of a proton.

fission: process of splitting a heavy atom into smaller pieces

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

With the discovery of the neutron as a fundamental particle, many paradoxes of physics and chemistry were finally resolved, and new areas of research evolved. Prior to the discovery of the neutron as a fundamental particle, scientists generally believed that the nucleus was comprised of protons and "nuclear electrons." However, one could not explain, for example, the spin of nuclei with that model. Now, at last, theory could predict the properties of the nucleus quite well. Also, since neutrons are not repelled by the charge on the atomic nucleus, they interact easily with nuclei. Neutron scattering enables the determination of crystal structures by probing the positions of nuclei in a sample. Neutrons can also catalyze **fission** reactions, for example, the fission of uranium nuclei that led to the creation of nuclear power plants and the atomic bomb.

Only three years after the discovery of the neutron, Chadwick was awarded the Nobel Prize in physics in 1935. He was lured away from Cambridge to accept the chair in physics at Liverpool University, where he oversaw the construction of the first cyclotron in England. As World War II broke out, Chadwick played a prominent role in the effort to create the atomic bomb, both in England, and, beginning in 1943, as the leader of the British effort on the **Manhattan Project**. Chadwick returned to his chair in Liverpool in 1946, but soon thereafter he accepted an offer from his alma mater, the College of Gonville and Caius at Cambridge, to serve as its master, a post he held until his retirement in 1958. He died in Cambridge on July 24, 1974. SEE ALSO BERYLLIUM; NUCLEAR CHEMISTRY; RADIATION; RUTHERFORD, ERNEST.

Michael J. Fosmire

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Chalcogens

The chalcogens are the name for the Periodic Table group 16 (or V1). The group consists of the elements: oxygen, sulfur, selenium, tellurium, and polonium. The name of the group was proposed by Wilhelm Blitz and colleague Werner Fischer of the Institute of Inorganic Chemistry at the University of Hannover, Germany in 1932. The term "chalcogens" was derived from the Greek word *chalcos*, meaning "ore formers," since they all are be found in copper ores. Their compounds are referred to as "chalcogenides." These names became popular since they are analogous to the names of group 17(V11), halogens, meaning salt formers, and its compounds, halides. As an element oxygen is a gas while the other group members are solids. Both oxygen and sulfur can be found in pure form. All of the elements occur as ions in metal ores. The elements of this family have isotopes that vary in stability. Polonium is considered a radioactive element and to be handled with care.

The members of this group show increasing metal character as the atomic number increases. Both oxygen and sulfur are nonmetals, while selenium and tellurium are metalloids (both are semiconductors) and polonium is a metal. Bonding characteristics of these elements parallel their metal character. The smaller members of the group show a greater tendency to form covalent bonds than the larger members do. This is shown with the decrease of stability of H_2M compounds from H_2S to H_2Po.

Their electronegativities decrease with increasing atomic number (see table below). This trend explains the lessening of ionic character of the compounds of S - Po that are analogous to those of oxygen. It is for this reason, only oxygen can exhibit hydrogen bonding. This drastically changes the character of these compounds. If the boiling points of the H_2M compounds are compared, we find that the group shows this change in hydrogen bonding, since the smallest compound in weight has a boiling point almost 100° higher than any of the other group members.

Element	O	S	Se	Te	Po
Electronegativity	3.5	2.5	2.4	2.1	2.0
BP of H_2M	100.0°C	−59.55°C	−41.5°C	−2°C	

All of the elements can be found naturally as ions, most often as 2- ions (except for Po). Oxidation states of +2, +4, and +6 also can be found for members S - Po when combined with O, F, or Cl. The difference in oxidation states can be explained by the electronic structure of the elements. Oxygen is able to use only *s* and *p* orbitals for bonding. The larger members of the group use *d* orbitals in the hybridization and thus can participate in the use of an expanded octet. This is shown in compounds and complex ions such as: SOF_4, SF_4, $SeO_4{}^{2}-$, $TeF_8{}^{2}-$.

The elements and their compounds vary in their toxicity. It is interesting that oxygen and sulfur are essential to all life, while the compounds of selenium, tellurium, and polonium can be toxic. Selenium is an essential trace element even though at larger concentrations (above 5 ppm) it causes severe disorders. Tellurium compounds, while being toxic, have never been reported to cause a human fatality. Since polonium and its compounds are radioactive, they are considered extremely toxic in any concentration. SEE ALSO OXYGEN; POLONIUM; SELENIUM; SULFUR; TELLURIUM.

Catherine H. Banks

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Chappelle, Emmett

AMERICAN BIOCHEMIST
1925–

There are many ways that we could determine if there is life on other planets. The easiest method would be to look for aliens or any of the hallmarks

American biochemist Emmett W. Chappelle (l.), who used fluorescence in the detection of bacteria.

of civilization. But what if the life-form was microbial? Bacterial life may exist, but would we know it if we saw it?

Emmett Chappelle is a noted biochemist who has, among other accomplishments, devised a method for answering this question. Born on October 25, 1925, in Phoenix, Arizona, he received his B.S. in biochemistry from the University of California in 1950. From 1950 to 1953 he worked as an instructor in biochemistry at Meharry Medical College in Nashville, Tennessee. Chappelle received his M.S. in biochemistry in 1954 from the University of Washington and then returned to California, where he served as a research associate at Stanford University and as a scientist for the Research Institute of Advanced Studies at Stanford. In 1966 he began his work with the National Aeronautics and Space Administration (NASA) as an exobiologist and astrochemist. In 1977 Chappelle moved to the Goddard Space Flight Center as a remote sensing scientist.

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

His research with Grace Picciolo led to his invention of a method for the detection of **adenosine triphosphate (ATP)**. The technique takes advantage of the naturally occurring luciferase enzyme and the chemical luciferin. Both are obtained from the lantern of a firefly; hence, this technique is sometimes referred to as a "firefly bioluminescent assay." In combination with ATP and magnesium ions, luciferin and luciferase fluoresce, generating a light intensity that is proportional to the amount of ATP present.

photon: a quantum of electromagnetic energy

The advantage of fluorescence is that a properly constructed photomultiplier, under dark conditions, can detect the emission of a single **photon**, so it is possible to monitor for very low concentrations of ATP. The patented invention outlines how this fluorescence can be used for the detection of bacteria, particularly in a urine sample, thereby speeding the diagnosis of a bacterial infection.

However, such a technique can be applied to any determination of ATP. If extraterrestrial life exists, then there is the possibility that it will employ either ATP or a similar energy molecule. If that energy molecule is introduced into a firefly bioluminescent assay, then light will be produced and it can be measured. The detection of ATP or a similar molecule would be good evidence for the presence of extraterrestrial life.

More recently, Chappelle has been involved in the use of laser-induced fluorescence as a method for determining the health of forest vegetation. The photosystem of green plants uses fluorescence as one way to lose excess energy from absorbed photons, accounting for between 2 and 6 percent of the total absorption. Measuring the amount of fluorescence over a forest allows researchers to monitor the amount of **photosynthesis** that is occurring. This technique has two significant advantages: First it is nonintrusive and can be used with living plants. Second, it can be performed from within a low-flying airplane, allowing researchers to monitor remote areas.

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

For his work investigating the biochemistry of life, Chappelle has won numerous awards including NASA's Exceptional Scientific Achievement Medal. SEE ALSO Global Warming.

Todd W. Whitcombe

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Chardonnet, Hilaire

FRENCH CHEMIST
1839–1924

Louis-Marie-Hilaire Bernigaud, comte de Chardonnet, born in Besancon, France, is credited with having developed artificial silk, which came to be known as rayon. In the 1860s Chardonnet, originally trained as an engineer, assisted Louis Pasteur in an effort to save the French silk industry from an epidemic affecting silkworms.

In 1878, while working in a photographic darkroom, Chardonnet accidentally overturned a bottle of nitrocellulose. When he started to clean up the spill, he saw that the nitrocellulose had become viscous due to evaporation. As he wiped it, he noticed long, thin strands of fiber resembling those of silk.

Chardonnet began to experiment further with the nitrocellulose. He worked with the silkworm's food, mulberry leaves, turning them into a cellulose pulp with nitric and sulfuric acids, and stretched the resulting pulp into fibers. This fiber, cellulose nitrate, could be used in garments, but it was highly flammable. Some garments made of this early artificial silk reportedly burst into flame when a lit cigarette was nearby. Chardonnet solved this problem by denitrating these fibers with ammonium sulfide, which reduced the flammability of the material without sacrificing its strength.

French chemist Hilaire Chardonnet, who invented rayon.

Chardonnet received his first patent for artificial silk in 1884 and began manufacturing the material in 1891. In 1924 artificial silk came to be known as rayon. SEE ALSO CELLULOSE; FIBERS; PASTEUR, LOUIS; POLYMERS, SYNTHETIC.

Lydia S. Scratch

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Charles, Jacques

FRENCH MATHEMATICIAN AND PHYSICIST
1746–1823

Jacques-Alexandre-César Charles was a mathematician and physicist remembered for his pioneering work with gases and hydrogen balloon flights. Charles was born on November 12, 1746, in Beaugency, Loiret, France; his first occupation was as a clerk at the Ministry of Finance in Paris. However, his interests eventually turned to science.

In the late 1700s ballooning became a major preoccupation of France and other industrialized nations. In early June 1783 the Montgolfier brothers launched the first successful hot-air balloon in Paris. Charles, who was interested in aeronautics, understood the concept of buoyancy and also was aware of Henry Cavendish's discovery of hydrogen, an element some fourteen times lighter than air, seventeen years earlier. On August 27, 1783, Charles launched the first hydrogen-filled balloon using gas produced by the reaction of sulfuric acid on iron filings. Among the 50,000 witnesses of this event was Benjamin Franklin, then residing in Paris as the U.S. ambassador to France. When the balloon returned to Earth in the French countryside, it was reportedly attacked with axes and pitchforks by terrified peasants who believed it to be a monster from the skies. On November 21 of that same year the Montgolfier brothers launched the first hot-air balloon with humans aboard, managing an altitude of less than 30 meters (98 feet). Charles, with the aid of brothers Nicholas and Aine Jean Robert, became the first human to ascend in a hydrogen balloon just ten days later. A far greater height of almost 3,000 meters (9,843 feet) was attained thanks to the superior lift of the hydrogen balloon Charles had designed and helped build.

Charles is best known for his studies on how the volume of gases changes with temperature. The English scientist Robert Boyle had many years earlier determined the inverse relationship between the volume V and pressure P of a gas when temperature T is held constant. In 1662 he published the results that would later come to be known as Boyle's law ($V \alpha 1/P$ at constant T). During the winter of 1787 Charles studied oxygen, nitrogen, hydrogen, and carbon dioxide and found that the volume of all these gases increased identically with higher temperature when pressure was held constant ($V \alpha T$ at constant P). Charles did not publish the results of his work at the time, but another French scientist, Joseph-Louis Gay-Lussac, eventually learned of them. When Gay-Lussac did more extensive and precise experiments and published his similar findings in 1802 (as did the English scientist John Dalton), he acknowledged Charles's original work. Thus, the law governing the thermal expansion of gases, although sometimes called Gay-Lussac's law, is more commonly known as Charles's law.

While most of Charles's papers were on mathematics, he was ultimately an avid scientist and inventor. He duplicated a number of experiments that Franklin and others had completed on electricity and designed several instruments, including a new type of hydrometer for measuring densities and a reflecting goniometer for measuring the angles of crystals. Charles was elected to France's Academy of Sciences in 1785 and later became professor of physics at the Conservatoire des Arts et Métiers. He died in Paris on April 7, 1823. SEE ALSO Boyle, Robert; Cavendish, Henry; Dalton, John; Gay-Lussac, Joseph-Louis.

David A. Dobberpuhl

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Chemical Engineering

Chemical engineers combine the science of chemistry with the discipline of engineering in order to manufacture materials and products essential to modern society. They are involved with the full scale of processes from the laboratory bench to the **pilot plant** and eventually at the manufacturing facility.

pilot plant: intermediate stage of testing for a chemical process to determine if it is industrially viable; between bench-top and production scale

How does chemical engineering differ from chemistry? Chemists discover the chemical reactions by which useful products may be made. Chemical engineers discover the processes and develop the equipment that allows the chemical reactions to work economically. The academic training of chemical engineers provides a strong background for a variety of areas, including:

- Process design
- Production engineering
- Research and development
- Safety
- Marketing/technical sales
- Environmental and waste management

Chemical engineering is particularly adaptable to solving the technological problems of modern society. Therefore, chemical engineers are often employed by the government and industrial firms. They make invaluable contributions to an improved quality of life by producing pharmaceutical products to cure diseases, fertilizers and pesticides to help feed a growing population, fabrics to clothe us, and petroleum products to warm our houses and move our cars. Chemical engineers also are deeply involved in preventing and treating pollution.

In addition to these key areas, chemical engineers are actively developing advanced materials used in the communications and space industries, food and beverage industries, and modern electronics.

The Laboratory versus a Plant Setting

It is instructive to examine some differences between chemical processes conducted in a laboratory setting compared to those larger-scale operations completed at either a pilot plant, where the process is conducted with intermediate-scale equipment used to optimze and scale up the process, or full-scale manufacturing facility. For example, the mixing of reactants in a small flask or beaker is easily accomplished using a magnetic stirrer or small mechanical stirrer. However, in an industrial process the phenomenon of uniform mixing is much more complicated, and specially designed agitators are required. Chemical engineers study the various mathematical models of mixing in order to design the most efficient mixing device.

Another example involves the heating of a reaction mixture. On a small scale, heating is accomplished using a hot plate or similar equipment, whereas on a large scale, heat exchangers are commonly used. The theory of heat transfer and the various designs of heat exchangers are topics studied by chemical engineers.

Another major difference occurring in a large-scale chemical plant is that fluids are being moved around from one unit to another. This requires special equipment such as pumps and valves and a knowledge of the fundamentals of transport phenomena and, in particular, fluid dynamics.

Chemical engineers are involved in a variety of different occupations within the general field of chemical engineering. The breakdown within the United States is as follows: process/production (30%); research and development (25%); sales/marketing (7%); education (4%); and other (13%).

A student interested in pursuing a career in chemical engineering should first of all be interested in mathematics and science, enjoy problem solving and troubleshooting, be decisive and innovative, and have excellent communication skills.

A Diverse Profession

In order to indicate the diverse nature of the chemical engineering profession, the typical work characteristics of different types of chemical engineers are examined.

First, let us consider chemical engineering research and development (R&D). The general objective in this area is to transform laboratory processes into commercial operations that are safe, efficient, and ecologically sound. Such engineers invariably work at the pilot plant level. They oversee the construction of the pilot plant, collect data, and decide whether the project should be taken to full scale. A research chemical engineer also collaborates with chemists in research laboratories. In addition to this, he or she works closely with the people who build the plants, namely, electricians, pipe fitters, boilermakers, and so forth. These chemical engineers also interact with specialists in industrial hygiene and safety, and waste disposal. The researcher spends a good deal of time analyzing and evaluating results, and transfers data to the process engineer and assists in the scale-up operations for commercial production.

Next, let us consider the chemical engineer in manufacturing (the so-called production engineer). This person is involved in producing a product in the required quality and quantity in a timely manner. This position requires exceptional leadership and interpersonal skills since one is interfacing with chemical operators on a routine basis. The production engineer (or plant manager) is also responsible for the safety of employees. In addition, a good deal of time is devoted to working with other departments, such as purchasing (raw materials), utilities (power), maintenance (repairs), marketing (production schedule), and research and process engineering (new and improved processes).

A third area involves the process engineer. This occupation concerns the scale-up of a process for commercial production. Here a chemical engineer will establish fundamental heat and material balances, develop working process flow sheets, and translate flow sheets into piping and instrument diagrams (PIDs). In addition, the process engineer has to specify the size of equipment and materials of construction. The types of equipment include reactors, distillation columns, heat exchangers, crystallizers, piping, and incinerators. This job involves close interactions with experts in chemistry, materials engineering, heat transfer, and computer simulation, to name a few. Also, the ability to work with mechanical, civil, and electrical engineers is very important. The process engineer assists as well with a plant startup.

Some chemical engineers choose to specialize in marketing and sales. These engineers are concerned with analyzing, developing, pricing, packaging, publicizing, and advertising. They must evaluate customer needs and also interact with production and R&D. In addition, it is vitally important that they understand all the details and properties of the product as well as its end uses. For this position one needs excellent people skills and a solid background in economics.

Current Trends

Prior to the 1970s, a large number of chemical engineers secured work in the booming petroleum industry and became involved in continuous processes. In more recent times, chemical engineers have entered many diverse fields—in particular, the pharmaceutical industry—working on the batch process level. Chemical engineers have also found employment with specialty chemical companies, as well as within the consumer and electronics industries.

Chemical engineers are actively involved in developing improved polymer processing and devices relevant to biomedical engineering. Another important research area is the physical and biological treatment of hazardous wastes. Computational methods are now used extensively in modeling studies, and computer simulation is routinely employed in plant design.

A further key area of interest involves separation techniques and technologies for solving separation problems in the chemical, environmental, food, pharmaceutical, and biotechnological industries.

Other exciting frontier areas of research in chemical engineering include molecular and nanoscale engineering, molecular simulation, surface modification, protein separation processes, supercritical fluid extraction, fluid particle systems, **catalysis** and reaction engineering, biochemical engineering, and computer-aided design. SEE ALSO CAREERS IN CHEMISTRY.

Reginald P. T. Tomkins

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

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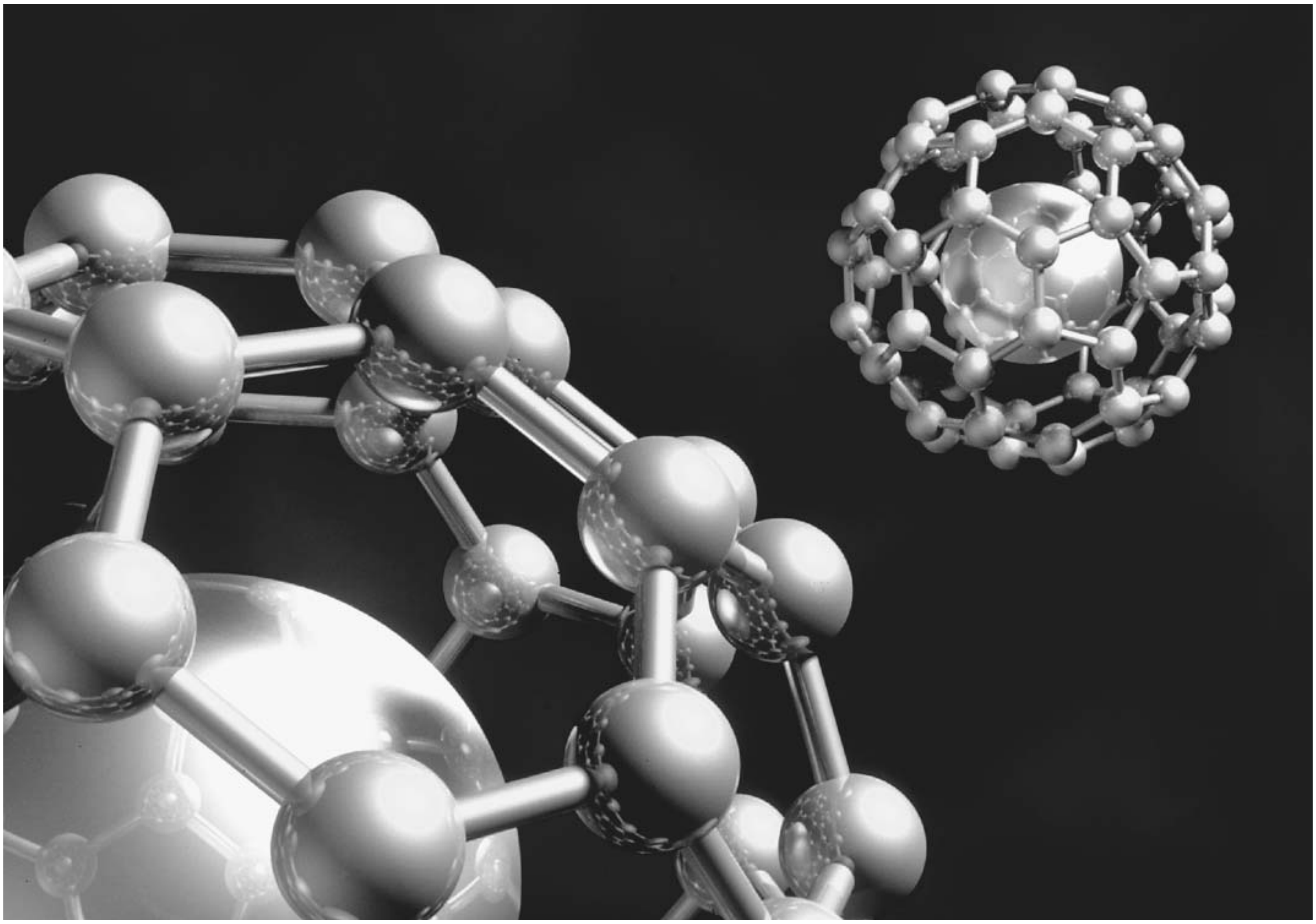
Chemical Informatics

As with many new disciplines, the field of chemical informatics has neither a precise name nor a clear definition. It is variously called cheminformatics, chemoinformatics, and molecular informatics, among other terms. Broadly defined, it encompasses the description, acquisition, visualization, management, and use of chemical information. A more narrow definition excludes the text-handling aspects of chemical information such as database searching and treats only the manipulation of two- and three-dimensional structural information. It is, however, generally agreed that cheminformatics (to use the currently most popular term) is indeed a legitimate new field in which chemistry and computer science intersect strongly. Those employed in this field develop new substances, materials, and processes by organizing, analyzing, and visualizing the information available to them. The present chief application of cheminformatics is in the field of drug discovery, but it is finding increasing acceptance and use in other applied areas of chemistry.

Although it derives its name and general focus from the slightly older field of bioinformatics, cheminformatics has its roots in a number of more established fields in chemistry, principally chemical information, chemometrics, and computational chemistry. The difference between cheminformatics and bioinformatics is mainly a matter of scale: bioinformatics is concerned mainly with data derived from the study of genes and large proteins, whereas cheminformatics focuses on small molecules. It emerged during the late 1990s from the convergence of two areas of chemistry that were earlier revolutionized by computer technology: the storage and retrieval of chemical data (generally referred to as chemical information), and the computational modeling of molecules and their behavior. An important aspect of this modeling had been the attempt to correlate structures of molecules with their biological activity, called qualitative structure-activity relationships (QSAR). More recently, the development of combinatorial chemical **synthesis** and high throughput screening (HTS) made possible the synthesis and testing of large numbers of compounds for drug testing—far more than could be handled by classical methods of analysis. The need to handle the resulting masses of data generated and the ability of modern computers to do so have hastened the development of cheminformatics in order to address the resulting glut of information. The most important current applications of cheminformatics are in the areas of molecular diversity analysis, the design of molecular libraries, and the virtual screening of potential drugs.

synthesis: combination of starting materials to form a desired product

Although the present focus of cheminformatics is mainly drug development, it has potential widespread applications in other areas, such as poly-



Computer-generated molecular structures.

mers, food science, and materials science. SEE ALSO Combinatorial Chemistry; Genome.

Bartow Culp

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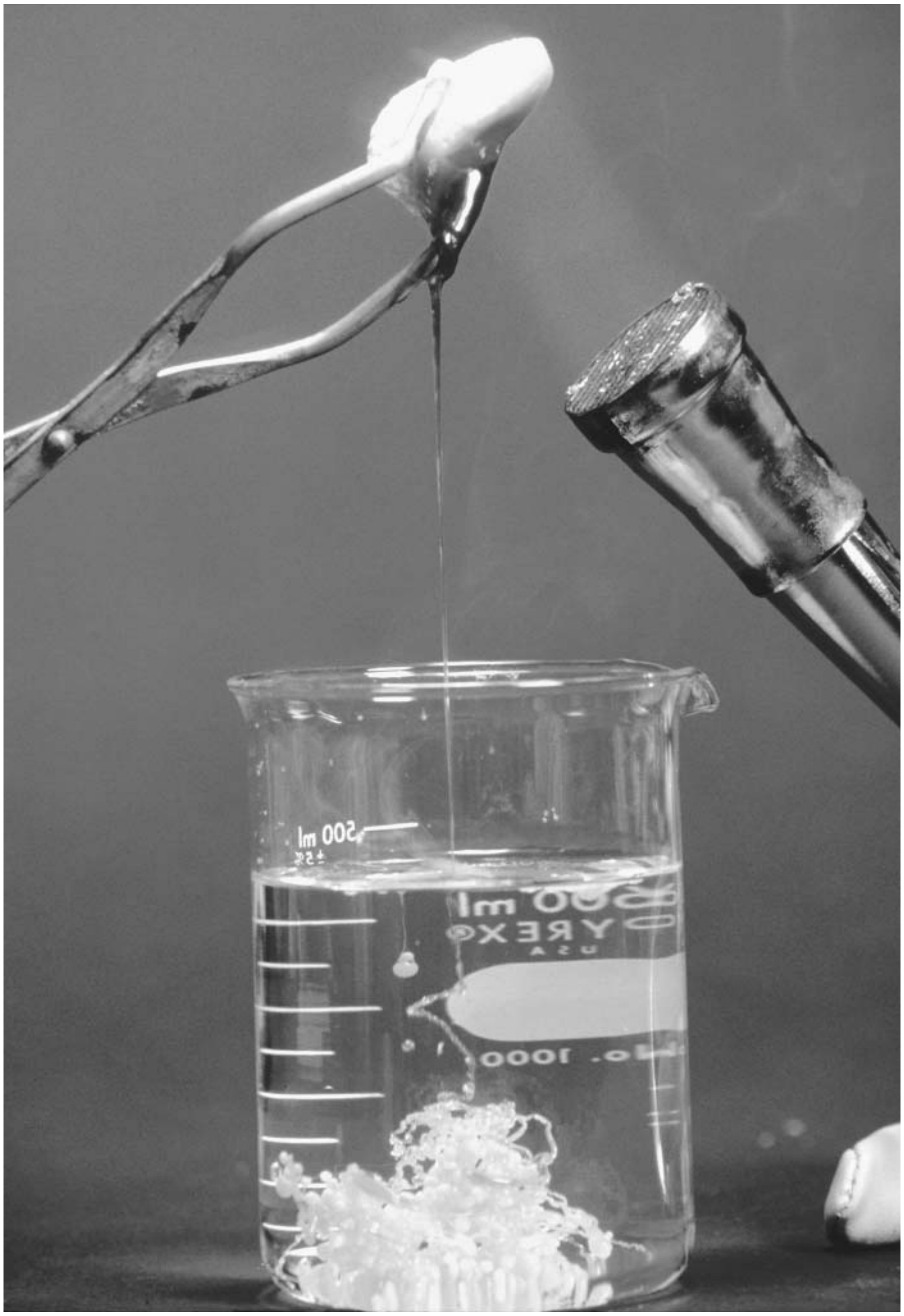
Chemical Reactions

A chemical reaction is a process in which one set of chemical substances (reactants) is converted into another (products). It involves making and breaking chemical bonds and the rearrangement of atoms. Chemical reactions are represented by balanced chemical equations, with chemical formulas symbolizing reactants and products. For specific chemical reactants, two questions may be posed about a possible chemical reaction. First, will a reaction occur? Second, what are the possible products if a reaction occurs? This



Sulfur reacting to heat.

entry will focus only on the second question. The most reliable answer is obtained by conducting an experiment—mixing the reactants and then isolating and identifying the products. We can also use periodicity, since elements within the same group in the Periodic Table undergo similar reactions. Finally, we can use rules to help predict the products of reactions, based on the classification of inorganic chemical reactions into four general categories: combination, decomposition, single-displacement, and double-displacement reactions.

Reactions may also be classified according to whether the **oxidation** number of one or more elements changes. Those reactions in which a change in oxidation number occurs are called **oxidation–reduction reactions**. One

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

oxidation–reduction reaction: reaction, sometimes called redox, that involves the movement of electrons between reactants to form products element increases its oxidation number (is oxidized), while the other decreases its oxidation number (is reduced).

Combination Reactions

In combination reactions, two substances, either elements or compounds, react to produce a single compound. One type of combination reaction involves two elements. Most **metals** react with most nonmetals to form ionic compounds. The products can be predicted from the charges expected for cations of the metal and **anions** of the nonmetal. For example, the product of the reaction between aluminum and bromine can be predicted from the following charges: 3+ for aluminum ion and 1− for bromide ion. Since there is a change in the oxidation numbers of the elements, this type of reaction is an oxidation–reduction reaction:

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

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

$$2Al\ (s) + 3Br_2\ (g) \rightarrow 2AlBr_3\ (s)$$

Similarly, a nonmetal may react with a more reactive nonmetal to form a covalent compound. The composition of the product is predicted from the common oxidation numbers of the elements, positive for the less reactive and negative for the more reactive nonmetal (usually located closer to the upper right side of the Periodic Table). For example, sulfur reacts with oxygen gas to form gaseous sulfur dioxide:

$$S_8\ (s) + 8O_2\ (g) \rightarrow 8SO_2\ (g)$$

A compound and an element may unite to form another compound if in the original compound, the element with a positive oxidation number has an accessible higher oxidation number. Carbon monoxide, formed by the burning of hydrocarbons under conditions of oxygen deficiency, reacts with oxygen to form carbon dioxide:

$$2CO\ (g) + O_2\ (g) \rightarrow 2CO_2\ (g)$$

The oxidation number of carbon changes from +2 to +4 so this reaction is an oxidation–reduction reaction.

Two compounds may react to form a new compound. For example, calcium oxide (or lime) reacts with carbon dioxide to form calcium carbonate (limestone):

$$CaO\ (s) + CO_2\ (g) \rightarrow CaCO_3\ (s)$$

Decomposition Reactions

When a compound undergoes a decomposition reaction, usually when heated, it breaks down into its component elements or simpler compounds. The products of a decomposition reaction are determined largely by the identity of the anion in the compound. The ammonium ion also has characteristic decomposition reactions.

A few binary compounds decompose to their constituent elements upon heating. This is an oxidation–reduction reaction since the elements undergo a change in oxidation number. For example, the oxides and halides of noble metals (primarily Au, Pt, and Hg) decompose when heated. When red solid mercury(II) oxide is heated, it decomposes to liquid metallic mercury and oxygen gas:

$$2HgO\ (s) \rightarrow 2Hg\ (l) + O_2\ (g)$$

halogen: element in the periodic family numbered VIIA (or 17 in the modern nomenclature) that includes fluorine, chlorine, bromine, iodine, and astatine

Some nonmetal oxides, such as the **halogen** oxides, also decompose upon heating:

$$2Cl_2O_5\ (g) \rightarrow 2Cl_2\ (g) + 5O_2\ (g)$$

Other nonmetal oxides, such as dinitrogen pentoxide, decompose to an element and a compound:

$$2N_2O_5\ (g) \rightarrow O_2\ (g) + 4NO_2\ (g)$$

Many metal salts containing oxoanions decompose upon heating. These salts either give off oxygen gas, forming a metal salt with a different nonmetal anion, or they give off a nonmetal oxide, forming a metal oxide. For example, metal nitrates containing Group 1A or 2A metals or aluminum decompose to metal nitrites and oxygen gas:

$$Mg(NO_3)_2\ (s) \rightarrow Mg(NO_2)_2\ (s) + O_2\ (g)$$

All other metal nitrates decompose to metal oxides, along with nitrogen dioxide and oxygen:

$$2Cu(NO_3)_2\ (s) \rightarrow 2CuO\ (s) + 4NO_2\ (g) + O_2\ (g)$$

Salts of the halogen oxoanions decompose to halides and oxygen upon heating:

$$2KBrO_3\ (s) \rightarrow 2KBr\ (s) + 3O_2\ (g)$$

Carbonates, except for those of the alkali metals, decompose to oxides and carbon dioxide.

$$CaCO_3\ (s) \rightarrow CaO\ (s) + CO_2\ (g)$$

A number of compounds—hydrates, hydroxides, and oxoacids—that contain water or its components lose water when heated. Hydrates, compounds that contain water molecules, lose water to form anhydrous compounds, free of molecular water.

$$CaSO_4 \cdot 2H_2O\ (s) \rightarrow CaSO_4\ (s) + 2H_2O\ (g)$$

Metal hydroxides are converted to metal oxides by heating:

$$2Fe(OH)_3\ (s) \rightarrow Fe_2O_3\ (s) + 3H_2O\ (g)$$

Most oxoacids lose water until no hydrogen remains, leaving a nonmetal oxide:

$$H_2SO_4\ (l) \rightarrow H_2O\ (g) + SO_3\ (g)$$

Oxoanion salts that contain hydrogen ions break down into the corresponding oxoanion salts and oxoacids:

$$Ca(HSO_4)_2\ (s) \rightarrow CaSO_4\ (s) + H_2SO_4\ (l)$$

Finally, some ammonium salts undergo an oxidation–reduction reaction when heated. Common salts of this type are ammonium dichromate, ammonium permanganate, ammonium nitrate, and ammonium nitrite. When these salts decompose, they give off nitrogen gas and water.

$$(NH_4)_2Cr_2O_7\ (s) \rightarrow Cr_2O_3\ (s) + 4H_2O\ (g) + N_2\ (g)$$

$$2NH_4NO_3\ (s) \rightarrow 2N_2\ (g) + 4H_2O\ (g) + O_2\ (g)$$

Ammonium salts, which do not contain an oxidizing agent, lose ammonia gas upon heating:

$$(NH_4)_2SO_4\ (s) \rightarrow 2NH_3\ (g) + H_2SO_4\ (l)$$

Single-Displacement Reactions

In a single-displacement reaction, a free element displaces another element from a compound to produce a different compound and a different free element. A more active element displaces a less active element from its compounds. These are all oxidation–reduction reactions. An example is the thermite reaction between aluminum and iron(III) oxide:

$$2Al\ (s) + Fe_2O_3\ (s) \rightarrow Al_2O_3\ (s) + 2Fe\ (l)$$

The element displaced from the compound is always the more metallic element—the one nearer the bottom left of the Periodic Table. The displaced element need not always be a metal, however. Consider a common type of single-displacement reaction, the displacement of hydrogen from water or from acids by metals.

The very active metals react with water. For example, calcium reacts with water to form calcium hydroxide and hydrogen gas. Calcium metal has an oxidation number of 0, whereas Ca^{2+} in $Ca(OH)_2$ has an oxidation number of +2, so calcium is oxidized. Hydrogen's oxidation number changes from +1 to 0, so it is reduced.

$$Ca\ (s) + 2H_2O\ (l) \rightarrow Ca(OH)_2\ (aq) + H_2\ (g)$$

Some metals, such as magnesium, do not react with cold water, but react slowly with steam:

$$Mg\ (s) + 2H_2O\ (g) \rightarrow Mg(OH)_2\ (aq) + H_2\ (g)$$

Still less active metals, such as iron, do not react with water at all, but react with acids.

$$Fe\ (s) + 2HCl\ (aq) \rightarrow FeCl_2\ (aq) + H_2\ (g)$$

Metals that are even less active, such as copper, generally do not react with acids.

To determine which metals react with water or with acids, we can use an activity series (see Figure 1), a list of metals in order of decreasing activity. Elements at the top of the series react with cold water. Elements above hydrogen in the series react with acids; elements below hydrogen do not react to release hydrogen gas.

The displacement of hydrogen from water or acids is just one type of single-displacement reaction. Other elements can also be displaced from their compounds. For example, copper metal reduces **aqueous solutions** of ionic silver compounds, such as silver nitrate, to deposit silver metal. The copper is oxidized.

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

$$Cu\ (s) + 2AgNO_3\ (aq) \rightarrow Cu(NO_3)_2\ (aq) + 2Ag\ (s)$$

The activity series can be used to predict which single-displacement reactions will take place. The elemental metal produced is always lower in the activity series than the displacing element. Thus, iron could be displaced from $FeCl_2$ by zinc metal but not by tin.

Figure 1. Activity series.

ACTIVITY SERIES

Li K Ba Ca Na	These metals will displace hydrogen gas from water
Mg Al Zn Fe Cd Ni Sn Pb	These metals will displace hydrogen gas from acids
H	
Cu Hg Ag Au	These metals will not displace hydrogen gas from water or acids

Double-Displacement Reactions

Aqueous barium chloride reacts with sulfuric acid to form solid barium sulfate and hydrochloric acid:

$$BaCl_2\ (aq) + H_2SO_4\ (aq) \rightarrow BaSO_4\ (s) + 2HCl\ (aq)$$

Sodium sulfide reacts with hydrochloric acid to form sodium chloride and hydrogen sulfide gas:

$$Na_2S\ (aq) + 2HCl\ (aq) \rightarrow 2NaCl\ (aq) + H_2S\ (g)$$

Potassium hydroxide reacts with nitric acid to form water and potassium nitrate:

$$KOH\ (aq) + HNO_3\ (aq) \rightarrow H_2O\ (l) + KNO_3\ (aq)$$

These double-displacement reactions have two major features in common. First, two compounds exchange ions or elements to form new compounds. Second, one of the products is either a compound that will separate from the reaction mixture in some way (commonly as a solid or gas) or a stable covalent compound, often water.

Double-displacement reactions can be further classified as precipitation, gas formation, and acid–base neutralization reactions.

Precipitation Reactions

Precipitation reactions are those in which the reactants exchange ions to form an insoluble salt—one which does not dissolve in water. Reaction occurs when two ions combine to form an insoluble solid or precipitate. We predict whether such a compound can be formed by consulting solubility rules (see Table 1). If a possible product is insoluble, a precipitation reaction should occur.

A mixture of aqueous solutions of barium chloride and sodium sulfate contains the following ions: Ba^{2+} (*aq*), Cl^- (*aq*), Na^+ (*aq*), and SO_4^{2-} (*aq*). According to solubility rules, most sulfate, sodium, and chloride salts are soluble. However, barium sulfate is insoluble. Since a barium ion and sulfate ion could combine to form insoluble barium sulfate, a reaction occurs.

SOME SOLUBILITY RULES FOR INORGANIC SALTS IN WATER

Compound	Solubility
Na^+, K^+, NH_4^+	Most salts of sodium, potassium, and ammonium ions are soluble.
NO_3^-	All nitrates are soluble.
SO_4^{2-}	Most sulfates are soluble. Exceptions: $BaSO_4$, $SrSO_4$, $PbSO_4$, $CaSO_4$, Hg_2SO_4, and Ag_2SO_4.
Cl^-, Br^-, I^-,	Most chlorides, bromides, and iodides are soluble. Exceptions: AgX, Hg_2X_2, PbX_2, and HgI_2.
Ag^+	Silver salts, except $AgNO_3$, are insoluble.
O^{2-}, OH^-	Oxides and hydroxides are insoluble. Exceptions: NaOH, KOH, NH_4OH, $Ba(OH)_2$, and $Ca(OH)_2$ (somewhat soluble).
S^{2-}	Sulfides are insoluble. Exceptions: salts of Na^+, K^+, NH_4^+ and the alkaline earth metal ions.
CrO_4^{2-}	Most chromates are insoluble. Exceptions: salts of K^+, Na^+, NH_4^+, Mg^{2+}, Ca^{2+}, Al^{3+}, and Ni^{2+}.
CO_3^{2-}, $PO4^{3-}$, SO_3^{2-}, SiO_3^{2-}	Most carbonates, phosphates, sulfites, and silicates are insoluble. Exceptions: salts of K^+, Na^+, and NH_4^+.

Table 1.

$$BaCl_2\ (aq) + Na_2SO_4\ (aq) \rightarrow BaSO_4\ (s) + 2NaCl\ (aq)$$

Gas-Formation Reactions

A double-displacement reaction should also occur if an insoluble gas is formed. All gases are soluble in water to some extent, but only a few gases [HCl (g) and NH_3 (g)] are highly soluble. All other gases, generally binary covalent compounds, are sufficiently insoluble to provide a driving force if they are formed as a reaction product. For example, many sulfide salts will react with acids to form gaseous hydrogen sulfide:

$$ZnS\ (s) + 2HCl\ (aq) \rightarrow ZnCl_2\ (aq) + H_2S\ (g)$$

Insoluble gases are often formed by the breakdown of an unstable double-displacement reaction product. For example, carbonates react with acids to form carbonic acid (H_2CO_3), an unstable substance that readily decomposes into water and carbon dioxide. Calcium carbonate reacts with hydrochloric acid to form calcium chloride and carbonic acid:

$$CaCO_3\ (s) + 2HCl\ (aq) \rightarrow CaCl_2\ (aq) + H_2CO_3\ (aq)$$

Carbonic acid decomposes into water and carbon dioxide:

$$H_2CO_3\ (aq) \rightarrow H_2O\ (l) + CO_2\ (g)$$

The net reaction is:

$$CaCO_3\ (s) + 2HCl\ (\mathrm{aq}) \rightarrow CaCl_2\ (aq) + H_2O\ (l) + CO_2\ (g)$$

Sulfites react with acids in a similar manner to release sulfur dioxide.

Acid-Base Neutralization Reactions

A neutralization reaction is a double-displacement reaction of an acid and a base. Acids are compounds that can release hydrogen ions; bases are compounds that can neutralize acids by reacting with hydrogen ions. The most common bases are hydroxide and oxide compounds of the metals. Normally, an acid reacts with a base to form a salt and water. Neutralization reactions occur because of the formation of the very stable covalent water molecule, H_2O, from hydrogen and hydroxide ions.

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

Recognizing the pattern of reactants (element or compound, and the number of each) allows us to assign a possible reaction to one of the described classes. Recognizing the class of reaction allows us to predict possible products with some reliability. SEE ALSO ACID-BASE CHEMISTRY; SOLUTION CHEMISTRY; THERMODYNAMICS.

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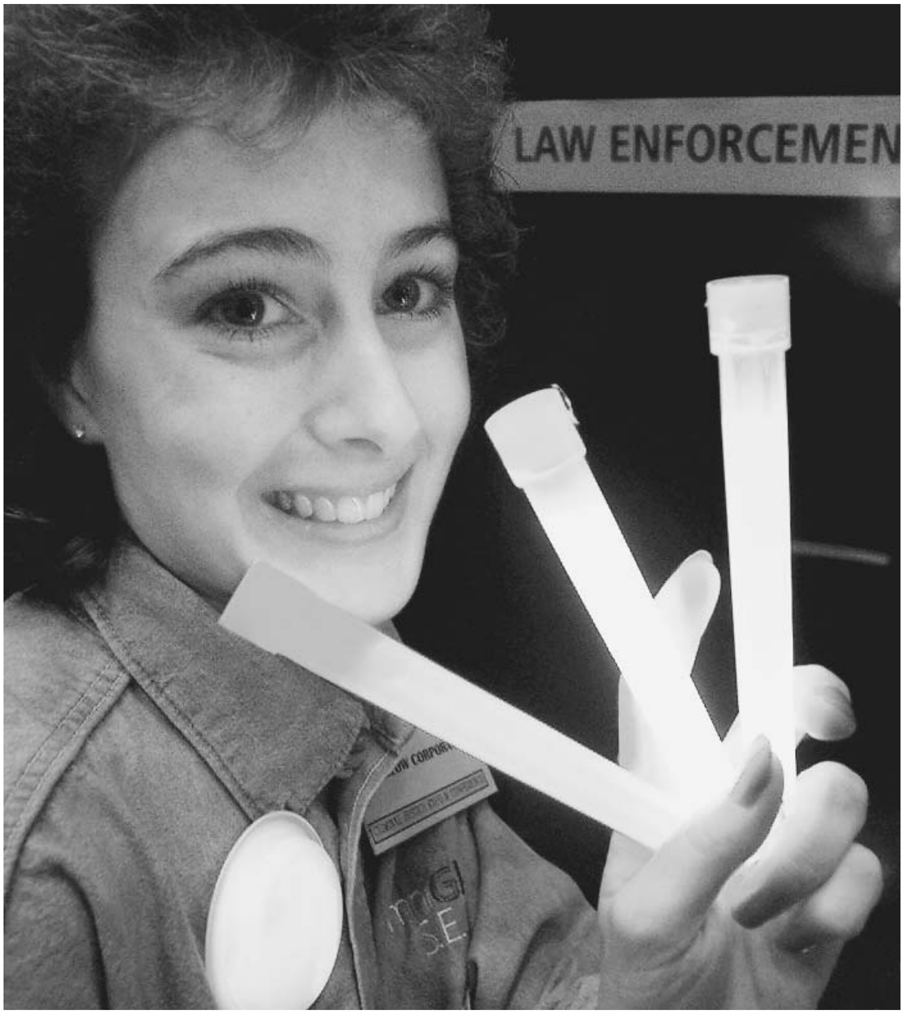
Chemiluminescence

When two molecules react chemically so that there is a release of energy (an exothermic reaction), that energy sometimes manifests itself not as heat but as light. This occurs because the energy excites the product molecules into which it has been funneled. A molecule in this excited state either relaxes to the ground state, with the direct emission of light, or transfers its energy to a second molecule, which becomes the light emitter. This process is referred to as chemiluminescence. The originally green, now multicolored, commercially made "light sticks" (often in the form of bracelets and necklaces) work in this way, utilizing the (exothermic) reaction of hydrogen peroxide with an oxalate **ester**. This **oxidation** reaction produces two molecules of carbon dioxide (CO_2), and the released energy is transferred to a fluorescent dye molecule, usually an anthracene derivative. Light sticks were developed by the U.S. Navy as an inconspicuous and easily shielded illumination tool for special operations forces dropped behind enemy lines. Besides their use as children's toys, they are also used extensively as a navigation aid by divers searching in muddy 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; a compound with the general formula $RC(O)OR^1$

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



These light sticks glow as a result of the energy released by a chemical reaction.

Chemiluminescence is also found in fireflies. The male firefly uses the reaction of a luciferin substrate and the enzyme luciferase with oxygen, with **adenosine triphosphate (ATP)** as an energy source, to create the illumination it uses to attract a mate. Because the detection of very minute amounts of light is possible, chemiluminescence and bioluminescence have become the basis of many sensitive analytical and bioanalytical techniques or assays used to quantify particular compounds in samples. Indeed, the use of these techniques is broad enough to justify the existence of a journal devoted to them, the *Journal of Bioluminescence and Chemiluminescence*.

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

In 1669 Hennig Brand, a German alchemist, was attempting to recover, by means of intense heat, the gold he hoped was lurking in human urine. The waxy white substance that he did retrieve, which glowed green when exposed to air, was in fact elemental phosphorus.

The emission of light observed by Brand was actually chemiluminescence. The light arises from PO_2 molecules in an excited state. This excited state of PO_2 is brought about by the reaction between PO and ozone, which are both **intermediates** in the fundamental reaction between oxygen in air and P_4 vapor evaporating from the solid white phosphorus. It is unfortunate that the chemiluminescent glow of phosphorus gave rise to the term

intermediate: molecule, often short-lived, that occurs while a chemical reaction progresses but is not present when the reaction is complete "phosphorescence." Scientifically, phosphorescence is a process whereby absorbed photons are emitted at a later time, as exemplified by the glow of a watch face in the dark after its earlier exposure to light.

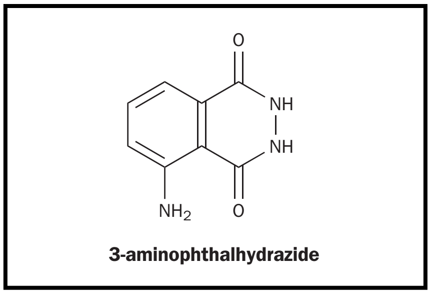


Figure 1. Structure of Luminol, 3-aminophthalhydrazide.

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

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

Luminol (3-aminophthalhydrazide) is used in a commercially available portable device called the Luminox that measures minute concentrations (parts per billion) of the pollutant nitrogen dioxide in air. Luminol is also used frequently in laboratory demonstrations of the chemiluminescence phenomenon. Luminol-mediated chemiluminescence is the result of an oxidation reaction. The oxidation proceeds in two steps, which ultimately lead to the production of the aminophthalate **anion** in an excited state and the elimination of water and molecular nitrogen. The formation of the strong triple bond (N≡N) is a major factor in the release of energy in the form of light.

Probably the simplest chemiluminescent reaction (and one that has been studied extensively) is the reaction between **nitric oxide**, NO, and ozone, O_3. The reaction (with about 10% efficiency) yields nitrogen dioxide in an excited state (NO_2^*)

$$NO + O_3 = NO_2^* + O_2$$

$$NO_2^* = NO_2 + h\nu$$

The reaction was developed in the early 1970s as a specific and instantaneous method to detect nitric oxide in the exhaust of automobiles. This use of chemiluminescence rapidly led to application of the same phenomenon to monitor the presence of NO in the atmosphere. Both applications continue in use. Ozone can easily be produced by passing dry air or oxygen through an electric discharge. The ozone-containing stream and the sample to be evaluated are mixed in a dark chamber adjacent to a photomultiplier tube, and the chemiluminescence signal that is produced is amplified. These devices are capable of monitoring NO levels ranging from parts per trillion to thousands of parts per million; an individual instrument can sometimes measure concentrations extending across six orders of magnitude.

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

The familiar yellow glow from a natural gas or wood-burning flame is not the result of chemiluminescence, but is due to bright, red-hot particles of carbon soot. The blue, green, and other colors produced when **metals** are put into flame can indeed be ascribed to chemiluminescence; in these instances the luminescence is accompanied by heat production.

According to information provided by the Harbor Branch Oceanographic Institution in Ft. Pierce, Florida, more than 90 percent of organisms living in the oceans at depths from 200 to 1,000 meters (656 to 3,281 feet) use chemiluminescence for activities such as attracting prey and avoiding predators. Light from the sky is quite weak at those depths; a fish that emits a dim glow from its lower parts could become invisible from below, while a fish without this capability would appear as a dark shadow. SEE ALSO Bioluminescence; Phosphorus; Radiation.

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Chemistry and Energy

Energy is central to our understanding of chemistry, for atoms adopt arrangements that correspond to the lowest possible energy and electrons in atoms adopt the lowest possible energy distribution. The adoption of lowest energy arrangements of atoms is responsible for the characteristic shapes of molecules. For instance, the tetrahedral shape of the methane molecule (CH_4) corresponds to the lowest energy arrangement possible for one carbon atom and four hydrogen atoms. The characteristic bond lengths in a molecule are the distances between centers of atoms corresponding to the atoms' lowest energy arrangement. The distribution of electrons in molecules—whether they are present as forming single, double, or triple bonds, or whether they do not participate in bonding at all—corresponds to the arrangement of lowest energy for those electrons.

Energy considerations are central to determinations of whether a reaction will run in one direction or another, but great care must be exercised in this regard for although most reactions run in the direction of decreasing energy (e.g., the **combustion** of a fuel), some reactions run in the direction of increasing energy (e.g., the decomposition of pure ammonia maintained at a high temperature). To determine the spontaneous direction of a reaction, it is necessary to consider, not the quantity of energy absorbed or released but its quality as measured by the change in entropy. This is the domain of the second law of thermodynamics.

combustion: burning, the reaction with oxygen

Energy changes are also used to identify materials and to explore their detailed structures. This is the domain of **spectroscopy**, in which molecules are excited to higher energy states by the absorption of energy in the form of electromagnetic radiation. In some materials, the excess energy of an excited state is emitted as radiation: this is the origin of fluorescence and phosphorescence, in which high frequency radiation (such as **ultraviolet radiation**) is absorbed and emitted as lower energy visible radiation.

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

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

When most people think of energy in connection with chemistry, however, they have in mind the production of energy for manufacturing, transportation, and the functioning of living organisms. The energy released by chemical reactions may be extracted as heat or as work. The ultimate source of the energy is the change in energy that accompanies the rearrangements of electrons and nuclei as atoms exchange partners. For instance, when a hydrocarbon fuel burns, the carbon–hydrogen and carbon–carbon bonds are replaced by the stronger carbon–oxygen and hydrogen–oxygen bonds of carbon dioxide and water, and the excess energy is released as heat. That is, at the high temperature of the reaction, the atoms are "loosened" from each other and allowed to adopt arrangements of lower energy.

The energy produced in a chemical reaction may also be extracted electrically. The device needed is called an electrochemical cell, which is a reaction vessel equipped with two electrodes. **Oxidation** (the loss of electrons) takes place at one electrode (the anode), and the electrons lost from the reactant are transferred to the electrode. They then travel through an external circuit, which might contain an electric motor, and re-enter the reaction vessel at the other electrode (the cathode), where they bring about reduction (the gain in electrons). In a primary cell, the reactants are sealed in at time of manufacture and the production of electricity continues until the

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 of products and reactants do not change

chemical reaction has reached **equilibrium**. In a secondary cell, an electric current is driven through the cell and reactants are formed at the electrodes. Once the cell is "charged," the newly formed reactants can be allowed to form products in the same way as in a primary cell. In a fuel cell, reactants are supplied continuously from the outside, and electricity is produced for as long as they are supplied.

feedstock: the raw materials necessary to carry out chemical reactions

The production of energy by any chemical reaction has potential consequences for the environment. Of greatest concern is the generation of carbon dioxide (CO_2) by the combustion of hydrocarbon fuels (the so-called fossil fuels—natural gas, coal, and petroleum). Carbon dioxide is a potent greenhouse gas and its accumulation in the atmosphere appears to be furthering global warming, with dire consequences for humanity. Fuel cells that use hydrocarbons as **feedstock** are also sources of pollution, as they form carbon dioxide, but they are more efficient, and less carbon dioxide is produced for a given supply of energy. Fuel cells may also operate using hydrogen as feedstock, in which case they produce only water, which has no impact on the already wet environment. However, the most economical supply of hydrogen is the burning of hydrocarbons, which produces the unwanted carbon dioxide. There is hope that photochemical sources of hydrogen will become sufficiently economical and eliminate the covert pollution step, but it is unlikely that sufficient energy can be achieved diurnally: fossil fuels represent the accumulation of years of solar energy.

nuclear: having to do with the nucleus of an atom

fission: process of splitting an atom into smaller pieces

Nuclear energy, which is obtained when nucleons (protons and neutrons) are allowed to adopt lower energy arrangements and to release the excess energy as heat, does not contribute to the carbon dioxide load of the atmosphere, but it does present pollution problems of a different kind: radioactive waste. Optimists presume that this waste can be contained, in contrast to the burden of carbon dioxide, which spreads globally. Pessimists doubt that the waste can be contained—for thousands of years. Nuclear power depends directly on the discipline of chemistry in so far as chemical processes are used to extract and prepare the uranium fuel, to process spent fuel, and to encapsulate waste material in stable glass blocks prior to burial. Nuclear fusion, in contrast to nuclear **fission**, does not present such serious disposal-related problems, but it has not yet been carried out in an economic, controlled manner.

Chemistry contributes in many ways to the more efficient and cleaner utilization of fossil fuels. Chemists find ways of extracting fuels from ever scarcer supplies; of promoting cleaner, more efficient combustion; and of producing cleaner exhausts through the development of catalysts. They are involved in the development of electrode materials for more efficient fuel cells, and in the development of photovoltaic systems to be used for more effective solar power generation. SEE ALSO Energy; Thermodynamics.

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Chemotherapy

Chemotherapy is the controlled use of chemicals for a medicinal purpose. The term was coined by the German bacteriologist Paul Ehrlich, around 1900, when he examined aniline dyes and arsenicals as possible treatments for diseases such as trypanosomiasis and syphilis. He envisioned "magic bullets" that could target invading organisms and leave the host unscathed. This goal of providing therapeutic benefits with minimal side effects continues in all areas of drug development. Remarkable successes have been obtained in compounds that modulate normal biochemistry within the human body. These include **analgesics**, antihistamines, cardiac rhythm regulators, blood pressure modifiers, anesthetics, anti-inflammatory agents, sedatives, diuretics, and vasodilators. In the battle against the unwanted growth of invading organisms and mutated cells (cancer), the greatest successes have occurred in the bacterial antibiotics; in the twentieth century they have increased human longevity more than any other medication. Similar successes for drugs treating viral infections and cancer have been elusive.

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

A young patient receiving a chemotherapy treatment.

In recent years chemotherapy has become a popular form of anticancer treatment. The goal of a magic bullet endures, but it is often difficult to attain because most of chemotherapy's useful agents are poisonous. This results from the similarities between cancerous cells and normal cells. Drugs that kill tumors are not specific enough to leave normal cells unharmed. Therefore, virtually all cancer chemotherapy is a delicate compromise between effectiveness and toxicity, resulting in significant side effects. Patients and physicians accept this because the alternatives are limited and the progression of the often fatal disease usually occurs more quickly without some intervening form of chemotherapy treatment.

The pursuit of chemical agents that can more effectively treat cancer has led to many decades of research by a multitude of chemists, biochemists, microbiologists, biologists, and research physicians. Thousands of chemicals have been synthesized and tested in tissue **cultures** and animal models. Only a modest number have proved to be useful in treating humans, but they have become the mainstay of the chemotherapeutic attack on cancer. In combination with early detection, surgery, radiation, and newly developing immunotherapies and targeted therapies, the judicious use of chemotherapy can kill tumors and limit their recurrence.

culture: living material developed in prepared nutrient media

Common Agents

The most active chemotherapeutic agents fall into a small number of broad categories depending on their mode of action: alkylating/cross-linking agents that interact with **DNA**; antibiotics that can kill mammalian cells instead of bacteria; antimetabolites/inhibitors that interfere with normal biochemistry; hormones that interact with **receptors** on tumor cells; and cytokines that can alter the balance of the intercellular communication system. Some commonly used agents, and their classifications, are listed in Table 1.

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

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

All these drugs, more generally, can be classified as either *reactive* or *interactive*. In the first case, biological activity depends on the chemical reaction of the drug with a target molecule. The resulting adduct interferes with normal cellular processes and may enhance cell death. Such reactive molecules are often indiscriminant, however, and are prone to powerful side effects. In the second case, biological activity depends only on the drug's structure, allowing it to interfere with cellular pathways that depend on lock-and-key recognition processes. These interactions can often be very specific, but may be limited in efficacy due to the existence of parallel pathways for most critical processes.

Reactions with DNA are prototypical of reactive anticancer chemicals. Alkylating and cross-linking agents such as nitrogen mustards, platinum compounds, alkane sulfonates, nitrosoureas, and methylating agents are believed to achieve their therapeutic effect by irreversibly binding to DNA and blocking its replication. This class of drugs is used routinely to treat most forms of cancer: sarcoma, carcinoma, teratoma, and leukemia.

Naturally occurring antibiotics (i.e., produced by other organisms) are complicated, multipurpose compounds. They often contain unsaturated polycyclic rings that can squeeze between DNA bases (intercalation) and interrupt DNA replication; quinone redox sites that can create free radicals

NAMES AND PROPERTIES OF ROUTINELY PRESCRIBED CHEMOTHERAPY AGENTS

Common Name	Primary Target	Mechanism	Similar Drugs
Alkylating Agents, Cross-linkers			
cyclophosphamide	DNA	nitrogen mustard (*reactive*)	ifosfamide melphalan
cisplatin	DNA	platinum coordination (*reactive*)	carboplatin
Antibiotics			
doxorubicin (adriamycin)	DNA	polycyclic rings allow intercalation (*interactive*), quinones allow redox reactions (*reactive*)	bleomycin mitomycin C daunorubicin
Antimetabolites, Inhibitors			
methotrexate	dihydrofolate reductase	mimics folate *interactive*)	trimetrexate
5-fluorouracil	thymdylate synthase, also incorporated into RNA and DNA	mimics deoxyuridine triphosphate (*reactive* and *interactive*)	5-azacytidine cytarabine 6-mercaptopurine
vincristine	microtubules	inhibits tubule assembly (*reactive*)	vinblastine
paclitaxel (taxol)	microtubules	inhibits tubule depolymerization (*reactive*)	docetaxel
etoposide	topoisomerase II	inhibits reconnection of DNA (*interactive*)	teniposide
topotecan	topoisomerase I	inhibits reconnection of DNA (*interactive*)	irinotecan
Hormones			
dexamethasone	glucocorticoid receptor	modify DNA transcription (*interactive*)	hydrocortisone prednisone cortisone
diethylstilbestrol	estrogen receptors	change hormonal balance (*interactive*)	estradiol modified estrogens
tamoxifen	estrogen receptors	blocks receptors in receptor-positive breast cancer (*interactive*)	torimenifene

SOURCE: Compiled from data contained in Perry, Michael C., ed. (2001). *The Chemotherapy Source Book,* 3rd edition. Philadelphia: Lippincott Williams & Wilkins.

Table 1. Names and properties of routinely prescribed chemotherapy agents.

in the cell; and electrophilic moieties that can alkylate the **guanine** of DNA. They are used routinely in the treatment of leukemia, germ cell tumors of the testis and ovary, lymphomas, and some childhood cancers.

Antimetabolites substitute for naturally occurring compounds in normal **metabolism** and **biosynthesis** reactions. They are designed to interfere with the normal biochemistry of a cell by deactivating or **retarding** enzyme action or by replacing normal nucleic acids in DNA and **RNA** with analogs that inhibit replication or repair. Special classes of **inhibitory** molecules include the microtubule-targeting drugs and topoisomerase inhibitors, which interfere with specific targets within a cell. They are used routinely in all forms of cancer, usually in combination with each other and with the alkylating/cross-linking agents.

Hormones and hormone receptor inhibitors can be administered because some tumors have hormone receptors. The response of the tumor to such therapy, however, is difficult to predict. It can be detrimental or beneficial depending on the hormone, the type of cancer, and even the individual. These drugs are used routinely to treat breast cancer patients with receptor-positive tumor types.

guanine: heterocyclic, purine, amine base found in 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)

biosynthesis: formation of a chemical substance by a living organism

retardation: to slow down a chemical reaction

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

inhibitory: relating to the prevention of an action that would normally occur

Cytokines, like hormones, are interactive molecules. They bind to receptors on either effector cells of the immune system or the tumor cells themselves. In doing so, they activate programs within the cells that may be useful at a particular time and location in killing the tumor or attracting immune killer cells. A special class of immune system cytokines, called interleukins, has been tested in melanoma and renal carcinoma with some encouraging results. Although cytokines are still largely experimental, their use is growing due to increased understanding of the complex signaling of the immune system.

Kinetics

excrete: to eliminate or discharge from a living entity

synthesis: combination of starting materials to form a desired product

To understand why chemical compounds are useful drugs in treating diseases like cancer, scientists study their complicated kinetics within the human body. The first concern is their rate of reaction or target binding affinities with other biological compounds. The second is their rate of distribution and **excretion**. Together, these are referred to as pharmacokinetics. This is part of a broader series of effects, referred to as pharmacodynamics, which include the positive and negative physiological changes induced by a drug. When a drug is administered (orally or by injection), it must reach the desired target in the organism before it is excreted or altered by detoxifying enzymes (usually located in the liver). Studies using radioactive forms of drugs have been used as tracers to follow both the chemical modifications and their distributions in various compartments of the body. Results have allowed the **synthesis** of new drugs with better chemistries, distributions, and toxicity profiles.

The most useful reactive drugs are those that have biologically relevant reaction rates. This means that they react slowly enough to reach their targets but fast enough to damage target cells before they are cleared. This appears to be a simple concept for drug design, but the immense number of reactions that can occur in a biological environment have made the discovery and development of such drugs a tedious procedure.

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

A successful strategy for achieving this kinetic balance is to use a compound that has a long-lived **intermediate** form which keeps it near its target. Two widely used drugs, cyclophosphamide and cisplatin, are good examples of this, but for different reasons.

In cyclophosphamide, the nitrogen mustard moiety of the parent compound is unreactive because the electron-withdrawing property of the ring reduces the reactivity of the lone pair of nitrogen electrons. The result is a drug that is both nontoxic and nontherapeutic. As the drug circulates in the bloodstream, liver enzymes (cytochrome P450) oxidize the 4th position of the ring (see Figure 1). The 4-OH form undergoes nonenzymatic cleavage of the acyclic tautomer, forming a phosphoramide mustard. This last step occurs slowly enough for the 4-OH form to leave the liver and enter other cells. Once the charged product forms, it cannot escape the cells that it enters. The chloro-ethyl side groups then cyclize sequentially into highly reactive aziridinium forms, which attack and cross-link DNA, leading to cell death.

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

In cisplatin, the +2 **oxidation** state of the platinum atom forms four coordination bonds in a square plane. Each ammine supplies two electrons

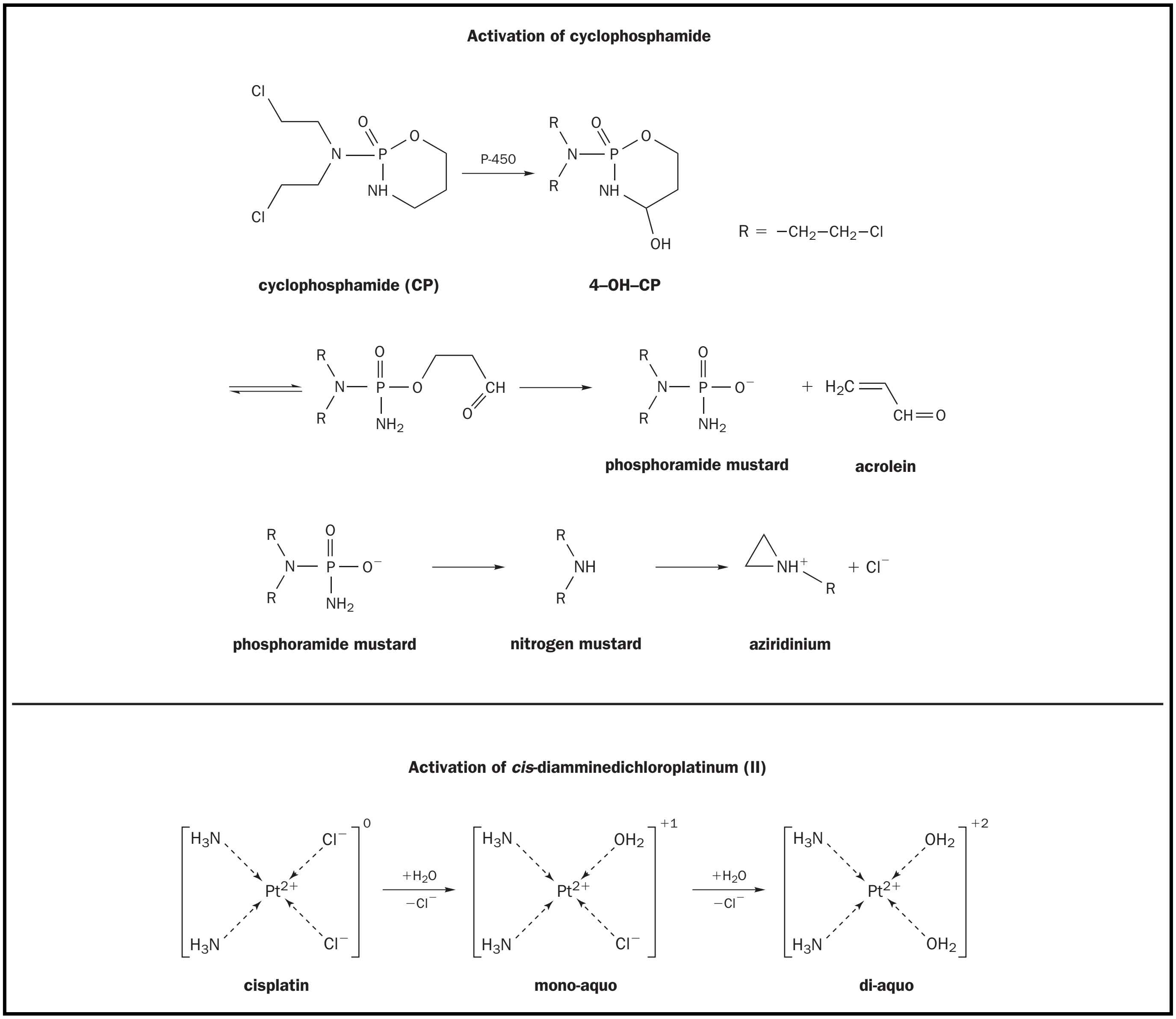

Figure 1. Activation reactions for the anticancer drugs cyclophosphamide and cisplatin.

from the filled orbital of nitrogen, while each chloride **anion** supplies two electrons and one negative charge that neutralizes the molecule. The result is a molecule stable to nucleophilic attack and able to cross cell membranes due to its charge neutrality. In the presence of low chloride, such as inside a cell, the chlorides begin to leave the platinum at a slow rate (a half-life of 5–6 hours). They are replaced by water molecules forming first mono-aquo and then di-aquo species, which are singly and doubly charged, respectively. These forms cannot penetrate the cell membrane and are confined inside the cell. Water makes a much better leaving group than Cl^-, resulting in rapid reactions with intracellular nucleophiles. With two sites of attack, the cross-linking of protein and DNA occurs readily.

In the case of interactive drugs, the most useful are those that exhibit long-term biological stability which allows them to reach their targets before they are degraded. They also have very high affinities for their targets

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

so they can block normal molecules from binding. Many of these have been extracted from fungi, bacteria, and plants. Years of evolution have fine-tuned these complex molecules into effective poisons that have been targeted against the predators of these organisms. In humans, many have shown remarkable antitumor properties with manageable toxicities. Others have been chemically modified to give them the necessary pharmacokinetic properties suitable for fighting cancer. It is believed that many more of these molecules remain to be discovered and that much will be learned by studying their mechanisms of action.

Specificity

Many successful drugs have shown specificity for certain tumors. The reason for this selectivity is usually not obvious, since the expected mechanisms of action often suggest that they would kill all cells equally well. In fact, many do harm normal cells, leading to the unpleasant side effects that most patients experience. Nonetheless, such drugs can be effective in reducing or eliminating large tumors while sparing the patient.

The specificity of a given drug for a particular tumor has largely been discovered by trial and error on patients enrolled in clinical trials. In many cases, the reasons for that specificity are still unknown but appear to result from the different biochemistries of tumor cells. In particular, the regulatory pathways in tumor cells are dramatically out of balance. This is often the result of several mutations in oncogenes and suppressor genes disabling the control elements of cell division and homeostasis. DNA replication accelerates and remains unwrapped longer, exposing it to more cross-linking. In some tumors, DNA repair enzymes are expressed at reduced levels, allowing damage to accumulate faster. There is also evidence that many active agents shift the unbalanced regulation of tumor cells into apoptosis (programmed cell death), causing the tumor to essentially commit suicide. These various lines of research show that although tumor cells are aggressive and uncontrolled, they are also vulnerable to the right kind of attack.

The continuing goal of mechanism-of-action and specificity research is to provide a better understanding of the interaction between drugs and tumor cells. This will allow the rational design of new drugs that are lower in toxicity and higher in effectiveness. As cellular targets are identified, as new proteins are characterized from the human genome project, as cell–cell communication pathways are elucidated, and as high-power computation is established, rational drug design will become more practical. Future chemotherapy will likely be targeted, individualized therapy, where patients will be fitted to therapies just as they would be to finely tailored clothes. SEE ALSO COORDINATION COMPOUNDS; EHRLICH, PAUL.

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Chevreul, Michel

FRENCH CHEMIST
1786–1889

French chemist Michel Chevreul, who established the melting point as a key criterion for the purity of a substance.

Michel-Eugène Chevreul was a chemist whose career spanned the greater part of the nineteenth century. He was born in Angers, France, on August 31, 1786, and died in Paris on April 9, 1889. Chevreul's father was a well-known physician. Raised in the midst of the terror of the French Revolution, Chevreul witnessed much violence and suffering. As a result, he maintained a lifelong aversion to politics and at an early age decided to devote his life to chemistry.

Chevreul's career as a scientist began at age seventeen when he became an assistant in the laboratory of Louis-Nicolas Vauquelin at the Muséum National d'Histoire Naturelle in Paris. While working in Vauquelin's laboratory, Chevreul began his study of organic chemistry with the investigation of the separation of natural coloring agents from their sources. At the age of twenty-four, he was named assistant naturalist at the museum. Chevreul then served as director of dyeing at the Manufacture Royale des Gobelins from 1824 to 1885. He became a member of the Academie des Sciences in 1826 and its president in 1839 and 1867. When Vauquelin retired, Chevreul attained the chair of chemistry at the museum, a position he held until his death in 1889.

Chevreul's career exemplifies the enormous strides made in the understanding of chemistry during the nineteenth century. He established the **melting point** as a key criterion for the purity of a substance. Even in the contemporary world, the melting point remains the first property determined to characterize a new solid. Chevreul excelled at the **elemental analysis** of organic substances and established the molecular formulas for many important chemical compounds. This procedure was considered very difficult in his time. His mentor, Vauquelin, had demonstrated that all foods are of four types: fats (**lipids**), proteins, starches, and sugars. In his continued studies of fats, Chevreul used the above procedures, along with various methods of purification for substances with animal origins, to identify several of the fatty acids as pure substances with consistent molecular formulas.

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

elemental analysis: determination of the percent of each kind of atom in a specific molecule

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

Chevreul also contributed to the improvement of the ancient art of soap making. He identified soaps as the potassium salts of the fatty oleic and

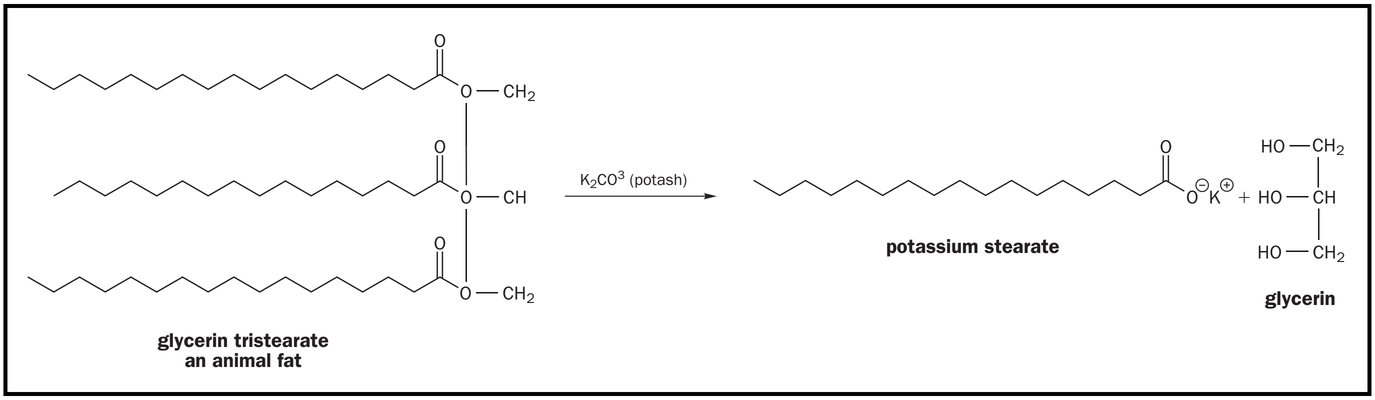

Figure 1. The saponification reaction.

stearic acids and animal fats from which soaps were derived as **esters** of the alcohol glycerol. This led to the replacement of potassium carbonate (**potash**) in soap manufacture with the cheaper and more reactive sodium hydroxide (lye), which became available commercially in the early 1800s. The reaction for the manufacture of soap, saponification, is shown in Figure 1. SEE ALSO Fats and Fatty Acids; Soap.

Lawrence H. Brannigan

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; a compound with the general formula RC(O)OR′

potash: the compound potassium oxide, K_2O

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Chirality

The term "chiral" (from the Greek for "hand") is applied to molecular systems whose asymmetry results in handedness; that is, the existence of a pair of nonsuperimposable mirror-image shapes (as illustrated by the relationship between one's right and left hands). Lord Kelvin coined the term "chirality" in 1884, (Eliel, p. 4) but it did not come into common usage until the 1960s. Many macroscopic examples of handed systems exist, including any object that features an inherent spiral or twist that can exhibit a left- and right-handed form: scissors, spiral staircases, screw threads, gloves, and shoes. Some mineralogical materials exhibit handedness in the solid state. In 1801 the crystallographer René-Just Haüy (1743–1822) observed that there were right- and left-handed quartz crystals, a phenomenon known as hemihedrism. The term "enantiomorphous" ("in opposite shape") was created to describe the macroscopic relationships between nonsuperimposable, mirror-image crystalline forms.

Optical Activity

The concepts of three-dimensional isomerism, or stereochemistry, resulted from the proposition of molecular chirality. In 1812 Jean-Baptiste Biot

(1774–1862), a physicist and a crystallographer, observed optical activity in mineralogical samples such as quartz, in which an asymmetrical crystalline form was macroscopically observable. In 1815 Biot also observed optical activity in samples of certain liquids, such as turpentine, various essential oils, and solutions of substances such as sugar and camphor. Because both pure liquids and solutions of organic compounds exhibit optical activity, the property could not be attributed to a characteristic of the solid state but instead had to be attributed to the molecular structure. In 1848 Louis Pasteur (1822–1895) separated an optically inactive sample of a tartaric acid salt into **optically active** dextrorotatory and levorotatory components by physically segregating the enantiomorphous crystalline forms. He showed that what had been thought to be a pure substance (racemic acid) was a mixture of two compounds: the natural, dextrorotatory tartaric acid and a substance that, although identical to the first compound identified in all of its other chemical properties, was yet opposite in its solid state structure and in its observed rotation of polarized light. In 1860 Pasteur proposed that molecular structural asymmetry was the basis for these observations. Jacobus van't Hoff (1852–1911) and Joseph-Achille Le Bel (1847–1930) independently proposed, in 1874, that molecular asymmetry and its consequences on isomerization could be explained if the arrangement (configuration) of the groups on a tetravalent atom was tetrahedral. Macroscopically or microscopically, a tetrahedral array of four different things gives rise to two and only two different arrangements that have a nonsuperimposable mirror-image (enantiomorphic) relationship (see Figure 1). In the case of molecular structures, these two shapes would be examples of enantiomers.

optically active: capable of rotating the plane of plane-polarized light

Representing Chiral Geometry

Asymmetrical atomic centers giving rise to stereoisomers have been known as chiral centers, although the more general terms "stereocenter" and "stereogenic center" have come into common usage since the 1980s. Asymmetrical tetrahedral atoms are only one example of what is meant by a stereocenter because the definition of the term encompasses a larger territory of structural characteristics. Over the years, a variety of representations have been used to depict the three-dimensionality of stereocenters. The representations in Figure 2 all depict the same sense of chirality for one of the two mirror-image arrangements (enantiomers) of 2-bromobutane.

Molecular Chirality

Chirality is a term that can be applied to molecular mixtures as well as to individual molecular species. Mixtures of chiral molecules can range from having 100 percent of the sample representing the same sense of asymmetry

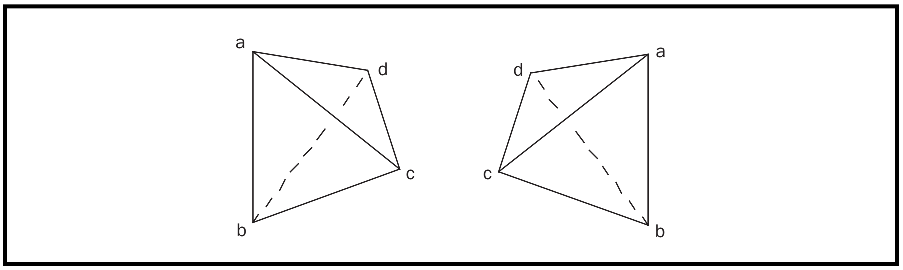


Figure 1. Nonsuperimposible mirror image arrangements for tetrahedra.

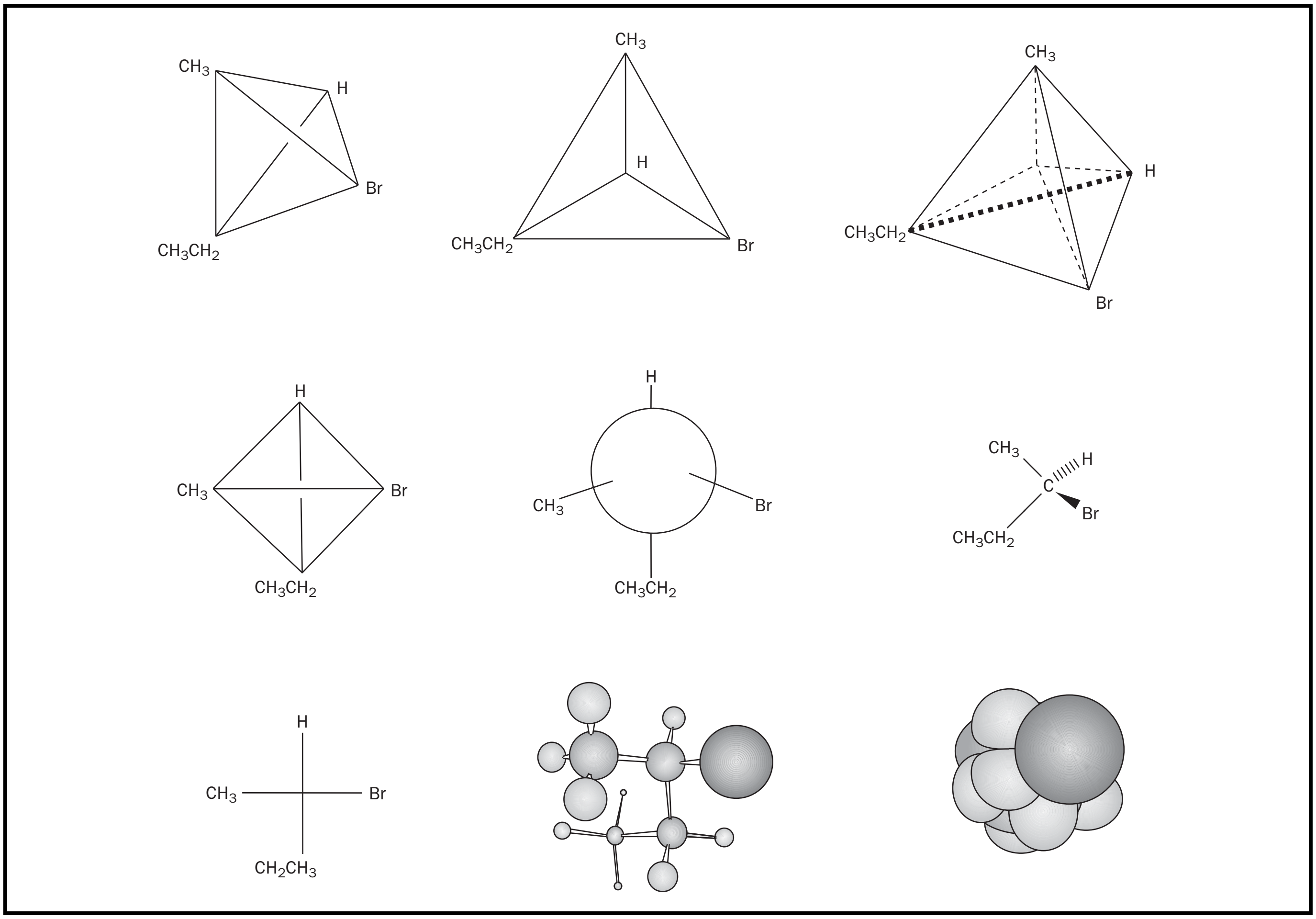


Figure 2. Representations for the three-dimensional geometry of a 2-bromobutane isomer.

(in which case the sample is a collection of homochiral molecules) to equal representation by molecules and their mirror-image isomers (in which case the sample is heterochiral or racemic), or any distribution inbetween (heterochiral and nonracemic). Extended tetrahedra (see bottom of Figure 3) are representative of molecules with an axis of chirality rather than a center of chirality. Molecular chirality results from one degree or another of twisting within a molecular structure, whereby a "turn to the left" can be distinguished from a "turn to the right." Even a simple stereocenter or an allene, when viewed from a certain perspective, presents a molecular twist that emerges as a common theme in the three-dimensional structure of chiral geometries (see Figure 3).

Restricted rotation in biphenyls (see Figure 4) creates another example of molecular chirality, which is called atropisomerism (literally "not turning," a reference to the restricted rotation). In other cases, the overall molecular architecture causes a twist of one sense or another to form. In helicenes, the simple interconversion realized by having one end of the molecule move past the other is restricted, and this results in isolatable chiral substances (see Figure 5). Different molecular geometries resulting from the bond rotations in butane, on the other hand, interconvert on a fast timescale at extremely low temperatures. The three staggered geometrical forms for rotation about the C2–C3 bond in butane are shown in Figure 6. Two of

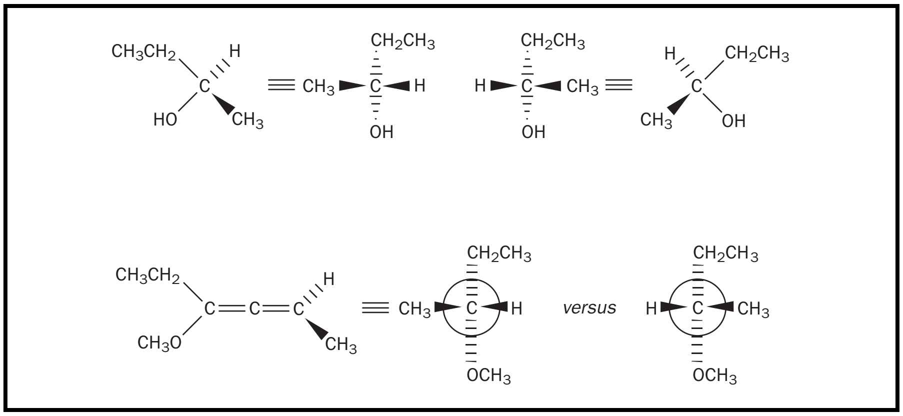


Figure 3. Examples of molecular twists present in chiral substances.

the conformational isomers of butane are chiral whereas the third is not. Molecular chirality can be examined by considering the definition. A molecular geometry that results in the possibility of a nonsuperimposable mirror image is chiral, but a superimposable mirror image renders the object achiral. The third conformational isomer shown in Figure 6 has a mirror plane of symmetry and a superimposable mirror image. It is achiral.

Stereoisomers: Enantiomers and Diastereomers

The two categories into which stereoisomers can be placed are absolutely distinctive in definition. Two stereoisomers that have a nonsuperimposable mirror-image relationship 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. Conformational stereoisomers, on the other hand, are most commonly diastereomeric. Molecules with two dissimilar stereocenters as the source of stereoisomerism can exist as one of

Figures 4, 5, and 6.

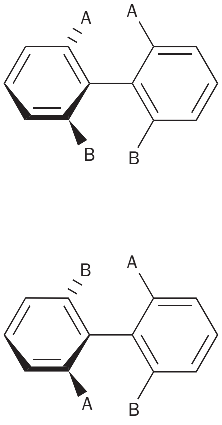


Figure 4. Biphenyl

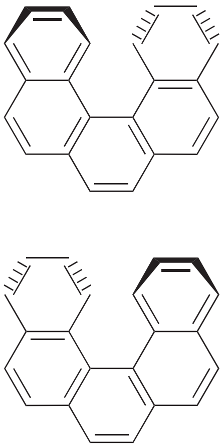


Figure 5. Helicene

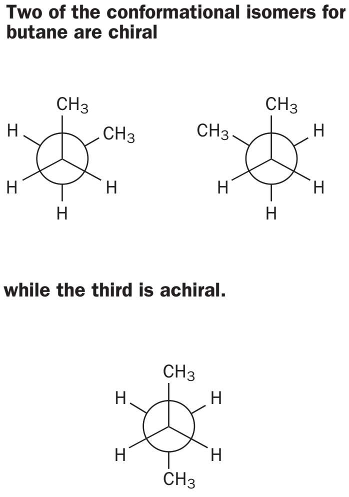


Figure 6. Butane

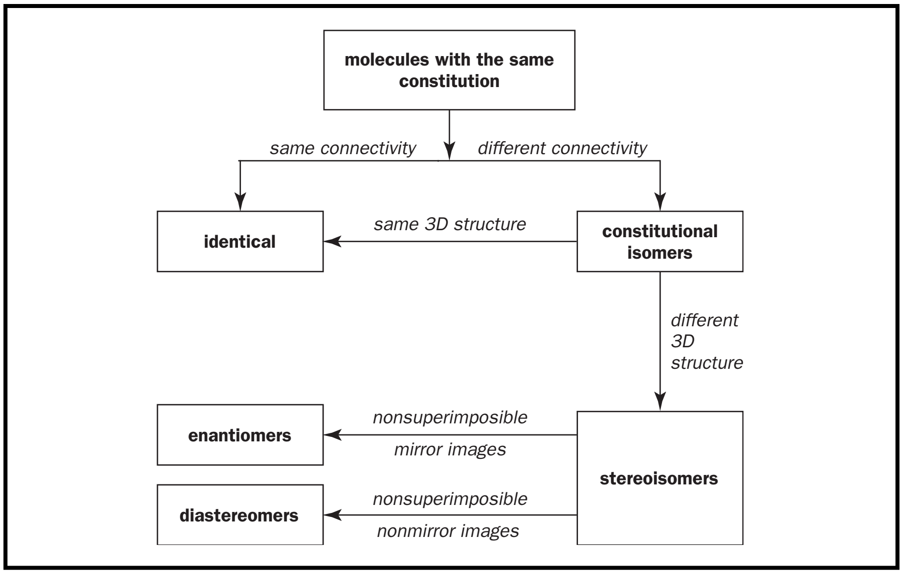
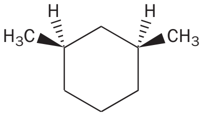
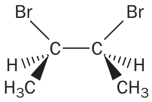


Figure 7. Schematic relationship between isomers.

four stereoisomers. Figure 8 outlines the relationships among these four stereoisomers.

As the number of stereocenters in a molecule increases, the number of possible diastereomers increases. A molecule with four dissimilar stereocenters, for example, can exist as one of sixteen stereoisomers. Of these sixteen stereoisomers there are four pairs of enantiomers, and the remaining four pairs are diastereomers. Molecules with configurational diastereomers also arise from many systems other than those with stereocenters. One of the most common examples is a double bond that is substituted in such a way that diastereomers exist. Any combination of two or more molecular features that give rise to stereoisomers will always produce diastereomers, whereas sources of chirality are needed to produce enantiomers. Because stereochemistry can have a high impact on molecular properties, diastereomers generally have easily discernable differences in their physical and chemical behaviors. Some molecules possess greater than or equal to two tetrahedral stereocenters and are nonetheless achiral. These are called meso stereoisomers. These occur when the internal symmetry of the molecule makes it superimposable on its mirror image.





Distinguishing Enantiomers

From 1874 to 1951 there was no experimental method that could be used to distinguish one enantiomeric form from the other. The physical property of optical activity formed the first basis on which labels were made. Naturally occurring (+)-glyceraldehyde [$HOCH_2CH(OH)CHO$] was usually used as the point of reference. Whatever its actual three-dimensional geometry, natural (+)-glyceraldehyde was assigned the designation (D), which stood for the configuration of dextrorotatory glyceraldehyde, and not for its optical rotation, which was designated as *d*- or (+). Optically active

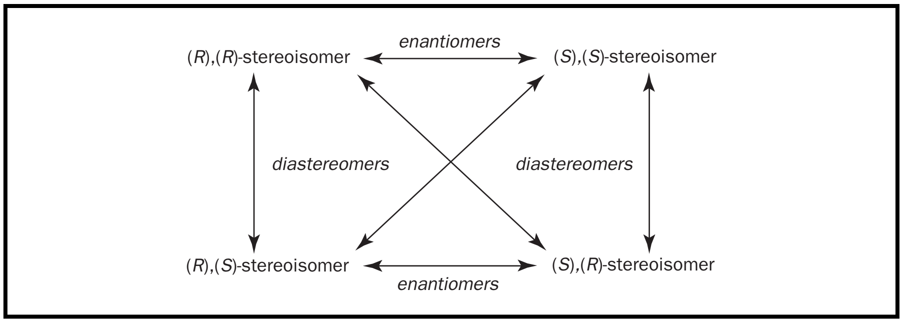


Figure 8. Schematic relationships for molecules with two different stereocenters.

molecules with single stereocenters of unknown configuration were, by precise chemical transformations, derived from or transformed into (D)-(+)-glyceraldehyde. In 1951 J. M. Bijvoet, A. F. Peerdeman, and A. J. van Bommel showed, using x-ray crystallography, that the absolute arrangement of atoms in space for sodium rubidium tartarate could be determined.

Enantiomers, and handed objects in general, can be distinguished only in a chiral environment. While a table-top (an achiral environment) interacts equally well with a left- or a right-handed glove, your own left hand (a chiral environment) can distinguish between these two chiral objects extremely easily. Plane-polarized light is comprised of equal intensities of right- and left-handed (hence, chiral) components. The interactions between these two components with inherently asymmetrical substances are unequal and give rise to the phenomenon of optical activity. In biochemical systems, enzymes represent a common chiral environment that can distinguish one enantiomeric form from another. Olfactory **receptor** sites and taste buds are also thought to be chiral because there are many examples of enantiomeric substances that can be distinguished by them. The two carvone enantiomers are the primary odor constituents of caraway and spearmint. Most of the naturally occurring amino acids are bitter tasting, whereas their enantiomers are sweet. In an achiral environment, the interactions and interactional energetics for enantiomers are identical and cannot be distinguished.

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

Separating Enantiomers

The majority of naturally occurring (plant and animal) substances for which stereoisomers are possible exist in nature as single enantiomers. The biochemical pathway used by one's body to synthesize cholesterol results in forming only a single stereoisomer, even though its connectivity represents a total of 128 possible stereoisomers. Because laboratory chemical reactions are not usually conducted in chiral environments, they will produce 1:1 (racemic) mixtures of enantiomers. Because only one enantiomer of a pharmaceutical (drug) is likely to be therapeutically active, chemists have devised strategies for preparing chemical compounds of only one enantiomer. These strategies are: (1) physical separation by temporarily converting the two enantiomers into two diastereomers (called resolution); (2) physical separation in a chiral **chromatographic** environment; (3) chemical discrimination in a chiral environment (using enzymes or other chiral platforms as chemical **reagents**); and (4) asymmetric **synthesis** of one enantiomer in preference to the other. Asymmetric chemical synthesis is extremely important because it allows chemists

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 extent to which the various components are absorbed by the stationary phase

reagent: chemical used to cause a specific chemical reaction

synthesis: combination of starting materials to form a desired product to produce new chiral drug candidates, such as single enantiomers of non-naturally occurring amino acids. SEE ALSO Isomerism; Le Bel, Joseph-Achille; Pasteur, Louis; van't Hoff, Jacobus.

Brian P. Coppola

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17
Cl
CHLORINE
35.453

Chlorine

MELTING POINT: $-101.5°C$
BOILING POINT: $-34°C$
DENSITY: 3.214 g/cm^3 (liq. at 0°C)
MOST COMMON IONS: Cl^{1-}, Cl^{1+}, Cl^{3+}, Cl^{5+}, Cl^{7+}

Chlorine is one of the **halogen** family of elements and the first of that family to be discovered. Swedish chemist Carl Wilhelm Scheele produced chlorine in 1774 by the reaction of manganese dioxide (MnO_2) with a solution of hydrochloric acid (HCl). In 1810 English chemist Sir Humphry Davy determined chlorine to be an element and named it for the color of the gas (the Greek word *chloros* means "pale green").

halogen: element in the periodic family numbered VIIA (or 17 in the modern nomenclature) that includes fluorine, chlorine, bromine, iodine, and astatine

Elemental chlorine is a diatomic molecule and is toxic. It has a high electronegativity that is about equal to that of oxygen. The most common **oxidation** numbers are 7, 5, 3, 1, and −1.

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

Chlorine is the most abundant of the halogens having a concentration of 19.87 parts per thousand (ppt) by weight in seawater and an average of 0.17 ppt in Earth's crust. It is produced commercially by electrolysis of seawater and brines. Sodium chloride (NaCl), or common table salt, can be obtained from seaside evaporation pools or mined from underground deposits.

Chlorine and its compounds have a large number of everyday uses. Chlorine is used in water purification as well in the production of safe plumbing components constructed of polyvinyl chloride (PVC). Chlorinated dyes, medicines, pesticides, disinfectants, and solvents have widespread applications. **Chlorofluorocarbon** compounds (CFCs) were once widely used as refrigerants, solvents, foaming agents, and spray-can propellants, but are now banned by international agreement due to the role of those compounds in the depletion of Earth's protective ozone layer. Chlorine was used during World War I (1914–1918) as a chemical warfare agent. SEE ALSO Bleaches; Davy, Humphry; Scheele, Carl.

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

John Michael Nicovich

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Cholecalciferol

Cholecalciferol is known as **vitamin** D_3. As early as 1870 people knew there was something in cod-liver oil that prevented rickets, a disease resulting in soft, deformed bones as a result of calcium deficiency. Sir Edward Mellanby contributed significantly to the understanding of the role of vitamin D: “It was in 1919/20,” cites a University of California study, “that Sir Edward Mellanby, working with dogs raised exclusively indoors (in the absence of sunlight or ultraviolet light), devised a diet that allowed him to unequivocally establish that the bone disease rickets was caused by a deficiency of a trace component present in the diet.” Mellanby is also credited with confirming that cod-liver oil could provide the missing vitamin. Calciferol was the second vitamin discovered that is soluble in fat; vitamin A was the first.

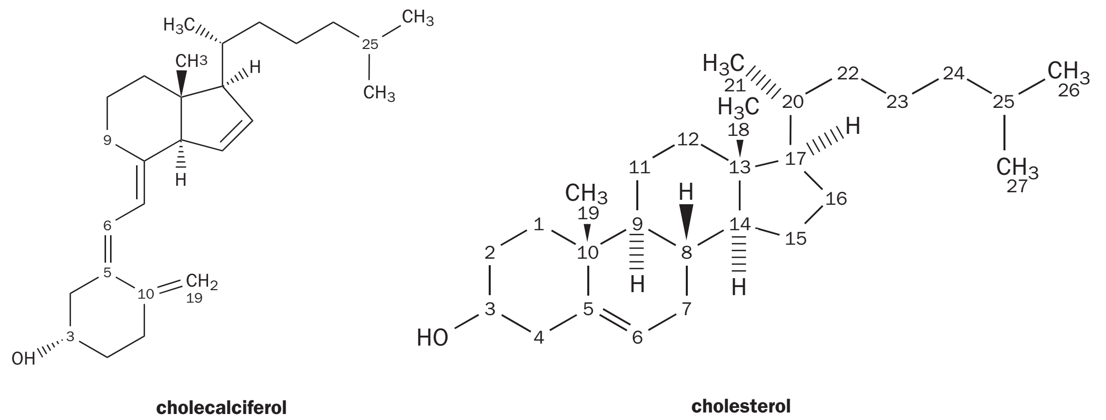
vitamins: molecules needed in small amounts for the normal function of the body; often used as part of an enzyme catalyzed reaction

Normally, it would seem unusual to expose food to ultraviolet (UV) radiation before trying to isolate a nutrient, but starting in the 1890s reports indicated that once exposed to high levels of sunshine, humans were unlikely to develop rickets. Scientists now know that UV exposure is essential for the body to produce cholecalciferol from cholesterol. See Figure 1 for the structures of cholesterol and cholecalciferol. Cholesterol is the steroid **lipid** often associated with heart disease when too much is present; small amounts of cholesterol are needed to make cholecalciferol and a host of other steroid hormones. Since humans can manufacture all the cholecalciferol needed for good health from exposure to sunshine, vitamin D is commonly referred to as the sunshine vitamin.

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

Vitamin D is involved in phosphorous and calcium **metabolism**. Cholecalciferol is converted into compounds that are directly involved in the absorption of calcium by the intestines. As with many steroid compounds, when cholecalciferol breaks down in the body, the resulting molecules are carried into the nucleus of certain cells and determine or change which genes are turned on or off. Recent reports suggest that the steroid hormone character of vitamin D may provide some anticancer activity.

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 which break down complex food molecules, thus liberating energy (catabolism)



cholecalciferol

cholesterol

Figure 1. Structures of cholecalciferol and cholesterol.

To help prevent vitamin D deficiency, most milk is now enriched with it. Other good sources of the vitamin are meat, poultry, fish, peanut butter, eggs, margarine, and liver, especially cod-liver oil. These sources exist in addition to the vitamin D produced naturally from exposure to sunshine. Unlike water-soluble vitamins, such as vitamin C, fat-soluble vitamins are stored in the liver and fat tissue and can become highly toxic if taken in excess. For these reasons, most nutrition experts do not generally recommend additional dietary supplements for vitamin D. Some individuals taking special medication for cholesterol, or who have dark skin (which reduces the ability of sunshine to produce vitamin D), may require a diet rich in vitamin D or a supplement. SEE ALSO CALCIUM; CHOLESTEROL.

David Speckhard

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Cholesterol

Cholesterol is the most abundant sterol in animal tissues, making up as much as 25 percent of cell membranes. Cholesterol may be found free or as part of cholesteryl **esters**. It is a **precursor molecule** for many steroid hormones, including **glucocorticoids**, **androgens** and **estrogen**, aldosterone, and mineralocorticoids. A major component of lipoproteins, it is also the precursor for bile salts and bile acids, which are necessary for digestion. Gallstones contain large amounts of cholesterol.

Cholesterol is a seventeen-carbon polycyclic compound made up of three six-membered and one five-membered fused rings. The molecule is relatively **nonpolar** and **hydrophobic**, but is slightly polar due to the presence of an alcohol **functional group**.

Plants contain no cholesterol. In animals cholesterol **synthesis** occurs in many cells, but most cholesterol synthesis occurs in the liver. Food products from animals contain cholesterol, and the average adult consumes around 450 milligrams (0.016 ounces) per day. Dairy products and egg yolks are particularly rich in cholesterol. Diets low in fat content and high in vegetables, especially those containing polyunsaturated **lipids**, can help to lower plasma cholesterol levels. Many physicians recommend that their patients try to maintain cholesterol levels below 200 milligrams per deciliter.

Cholesterol in blood plasma is conjugated with other lipid molecules and with carrier proteins. These lipoprotein complexes may form droplets called chylomicrons, but cholesterol is usually transported as part of a number of larger lipoproteins, including low density lipoprotein (LDL), which carries cholesterol from the liver to muscle and other tissues, and high density lipoprotein (HDL), which carries cholesterol to the liver for conversion to bile acids. Physicians are especially concerned when patients have high levels of LDL (the so-called bad cholesterol) in blood; moderate exercise and

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; a compound with the general formula $RC(O)OR^1$

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

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

androgen: group of steroids that act as male sex hormones

estrogen: female sex hormone

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

hydrophobic: relating to a region of a molecule that will, in solution with water, tend to be in contact with few water molecules; if an entire molecule is hydrophobic, it will not dissolve in water

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

synthesis: combination of starting materials to form a desired product

lipid: a nonpolar organic molecule; fatlike; one of a large variety of nonpolar hydrophobic (water-hating) molecules that are insoluble in water low-cholesterol diets help to increase HDL (the so-called good cholesterol). Either high fat intake or problems with the transport of cholesterol to and from cells can lead to atherosclerosis (hardening of the arteries), which in turn can contribute to heart attack (myocardial infarction) or stroke.

Humans do not oxidize cholesterol for energy. Instead, cholesterol is converted to bile acids such as cholic acid and deoxycholic acid in liver tissue. Bile acids and salts are secreted into bile, which passes into the intestine and emulsifies fats for digestion. Although some bile acids may be reabsorbed in the intestine along with lipids, much cholesterol leaves the body in feces in the form of **metabolites** such as bile acids and salts.

metabolites: products of biological activity that are important in metabolism

Diets rich in oatmeal or other vegetable products are believed to help to lower plasma cholesterol levels. Soluble fibers from the vegetable materials absorb cholesterol and help to prevent absorption in the intestine. SEE ALSO LOW DENSITY LIPOPROTEIN; STEROIDS.

Dan M. Sullivan

Chromium

MELTING POINT: 1,860°C
BOILING POINT: 2,670°C
DENSITY: 7.19 g/cm^3
MOST COMMON IONS: Cr^{2+}, Cr^{3+}, CrO_4^{2-}, $Cr_2O_7^{2-}$

24
Cr
CHROMIUM
52.00

Chromium was first identified in 1797 by the French chemist Louis-Nicolas Vauquelin, who isolated it from crocoite, a mineral also called Siberian red lead. The name for chromium is taken from the Greek *chroma*, which means "color." This is a fitting name, because chromium compounds are often found in vividly colorful shades of green, red, or yellow. As such, chromium compounds historically have found extensive use as pigments for paints. In contrast, elemental chromium is a shiny, hard, yet brittle, steel-gray **metal**. Since chromium is not found naturally in its free elemental state, it is usually extracted from chromite, $FeCr_2O_4$.

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

Perhaps the best-known use of chromium is as a decorative, protective, shiny plating over other metals, with chrome-plated automobile parts being a familiar example. Chromium is also an important **alloy** component in stainless steel because it makes the steel stronger and more corrosion-resistant. Paint pigments account for more than one-third of all chromium usage each year.

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

Overall, chromium is the twenty-first most abundant element in Earth's crust. It is usually found in the +2 (e.g., CrO), +3 (e.g., Cr_2O_3), or +6 (e.g., $K_2Cr_2O_7$) **oxidation** states, with chromic oxide, Cr_2O_3, being the ninth most abundant compound in Earth's crust. While chromium is considered a necessary micronutrient in human diets, many of its compounds are quite toxic. This is especially true of chromium in the +6 oxidation state, with compounds such as $K_2Cr_2O_7$ being identified as carcinogens. Thus chromium compounds should be handled carefully.

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

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Chromosome

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

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

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

A chromosome is a compactly folded complex of **DNA** and proteins containing many genes, found in the nuclei of **eukaryotic** organisms and in the nucleoids of **prokaryotic** organisms.

Each cell in an organism has a complete set of genetic information called a genome. Different organisms have different numbers of chromosomes in their genomes, ranging from a single chromosome in most bacteria to seventy-eight chromosomes in chickens. Humans cells have forty-six chromosomes, but these represent two sets of information as humans are diploid organisms; each cell has one information set inherited from the organism's mother and a second set inherited from its father. If an offspring inherits one X chromosome and one Y chromosome, he will be genetically male. If an offspring inherits X chromosomes from both parents, she will be genetically female.

Chromosomes consist of two kinds of molecules, deoxyribonucleic acid (DNA) strands and proteins. Chromosomes from eukaryotic organisms have linear DNA strands containing approximately fifty genes per millimeter, compared to 2,500 genes per millimeter in bacteria. Some of the noncoding DNA (DNA that does not **code** for proteins) is found in special structures at the ends of the chromosomes called telomeres. Much of the noncoding DNA in eukaryotic chromosomes may be involved in compacting the DNA into the highly organized chromosome structure. Some of this DNA has highly repetitive sequences and has been useful in forensic analysis.

code: mechanism to convey information on genes and genetic sequence

Proteins help to compact DNA: this is important because the DNA in a chromosome could not fit inside its cell if it were not compacted. Histones are positively charged proteins that neutralize negative DNA strands when they wrap around and form complexes with the DNA. This wrapped structure, called "beads on a string," represents the first level of compaction. The "beads" are condensed to form fibers, fibers fold into loops, loops combine with nuclear scaffold proteins to form rosettes, and rosettes condense to form coils. Finally, a chromatid with ten or more coils is formed. Nonhistone proteins within chromosomes are also important. These proteins have varied functions, including assisting in the unwinding of DNA and in the repairing of DNA.

Chromosomes from prokaryotic organisms have DNA strands that loop and form circles. The DNA in prokaryotic chromosomes forms complexes with histone like proteins that help to compact the DNA, link it to the cell membrane, and localize it in the nucleoid region of the cell. Some bacteria have extra chromosomal DNA—a mini-chromosome called a plasmid. Plasmids contain only a few genes but are rapidly exchanged among cells of a bacteria population. Plasmids have become useful tools in biotechnology and genetic engineering.

Recombination is a natural process of exchange of fragments of DNA strands between paired chromosomes, which happens occasionally during cell division. Genetic engineering techniques allow scientists to cut and paste DNA fragments from one source to another to produce recombinant chromosomes and transgenic organisms. SEE ALSO DNA REPLICATION; GENES; GENOME; PROTEINS.

David Speckhard

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Cleve, Per Theodor

SWEDISH CHEMIST
1840–1905

Per Theodor Cleve was a nineteenth-century expert in agricultural chemistry, inorganic and organic chemistries, geology, mineralogy, and oceanography.

Cleve's early schooling was in Stockholm, and after passing final examinations he went to Uppsala, Sweden, to study mineralogy and other sciences. Cleve earned a master's degree (M.Sc.) at the age of twenty-two years and completed his doctorate (Ph.D.) just one year later. During these years he received several travel grants that enabled him to visit laboratories in France, England, Italy, and Switzerland.

Some milestones of Cleve's teaching career at Uppsala University are: In 1860 the twenty-year-old student was appointed assistant professor in mineralogy; in 1863, at the age of twenty-three, he was named assistant professor in organic chemistry; and a year later he became professor of general chemistry and agricultural chemistry.

In Paris Cleve visited the research laboratory of chemist Charles-Adolphe Wurtz (1817–1884). The laboratory was unique in Europe in its attraction of young chemists, and here Cleve made many friends. Wurtz drew Cleve's attention to complex **metal** compounds. At age twenty-one Cleve published his first research paper on a complex chromium compound he had prepared and analyzed. In this paper he demonstrated that the compound was chromium trichloride-ammonia-water (in a 1:4:1 ratio). He later turned to the study of complex platinum compounds, of which he prepared hundreds. In 1872 Cleve, now thirty-two years old, published the results of this study in the *Transactions of the Royal Swedish Academy of Sciences.*

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

Cleve studied the group of elements known as the **lanthanide** elements. In 1879 he discovered two new lanthanide elements: holmium and thulium. The following year he undertook a thorough investigation of the newly discovered element scandium and proved that it had the properties predicted

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

by Dimitri Mendeleev years earlier with his discovery of the periodic law and his publication of *The Periodic Table.*

Cleve's most celebrated work in organic chemistry was the preparation and characterization of the isomeric aminonaphthalenesulfonic acids, today called Cleve's acids.

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

In 1894 Cleve was awarded the Davy Medal by the **Royal Society** in London. SEE ALSO HOLMIUM; LANTHANIDES; MENDELEEV, DIMITRI; SCANDIUM; THULIUM.

Ole Bostrup

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Clones

mitosis: process by which cells divide, particularly the division of the cell nucleus

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

A clone is an organism or cell derived asexually (through **mitosis**) from a single ancestor cell. The genetic content of the newer cell (or of any individual cell of the organism) is identical to that of the ancestor cell. In biochemistry a clone is a replica of all or part of a macromolecule, for example, deoxyribonucleic acid (**DNA**).

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

nuclear: having to do with the nucleus of a cell

The word "clone" originated in 1903 when it was proposed by Herbert J. Webber of the U.S. Department of Agriculture as a term to designate the offspring of plants propagated artificially (and asexually) via methods such as "rooting cuttings." Most clones occur naturally, as most organisms reproduce asexually. Most animals reproduce sexually, but many of the less complex **invertebrates** reproduce asexually, giving rise to clones. Currently, the terms "clone" and "cloning" are used in association with recent animal reproduction procedures (having both **in vitro** and **in vivo** stages) and the ability of scientists to alter the genetic makeup of organisms toward the greater benefit of humans in such areas as medicine and agriculture.

Reproductive cloning in higher animals, such as mammals, requires **nuclear** transfer, in which the entire genetic content of a cell is transferred to an embryonic cell that has been emptied of its genetic material. (Only 1 to 2 percent of these transfers are successful.) The most notable animal clone, the sheep Dolly, was born in 1997. She was the first animal to be cloned from the mature cell of another animal. Dolly was proof that a single, mature (fully differentiated) cell contains workable versions of all the genes necessary to produce an entire organism. In 2001 it was announced that human embryos, at the six-cell stage, had been produced via nuclear transfer.

expressed: in biochemistry—copied

Therapeutic cloning can involve recombinant DNA technology or molecular cloning. A segment of DNA from one organism (a vector) is introduced into the DNA of a second organism, yielding a hybrid or recombinant DNA molecule. The hybrid DNA molecule is then introduced into a host organism, in which it can be rapidly replicated and **expressed** to produce proteins of commercial or medical importance. The first such protein to be marketed commercially was human insulin, which is a small protein, having fewer than 100 amino acids, and which was "manufactured" in *Escherichia*

Two calves cloned from cells in cow's milk, Japan.

coli bacteria (the host organism). The first agricultural protein made from recombinant DNA, bovine growth hormone, was approved for use in 1994 and is given to approximately 25 percent of cows in the United States (its use is banned in the European Union). Other recombinant DNA products used in medicine include tissue plasminogen activator (TPA), used as an **anticoagulant** in the treatment of heart attack and stroke victims; factor VIII, a blood coagulant deficient in hemophiliacs; human growth hormone; interferons, used in the treatment of cancer; interleukins; monoclonal **antibodies**; and vaccines, such as hepatitis B vaccine.

anticoagulant: molecule that helps prevent the clotting of blood cells

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

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

Bacterial cells as host cells are not able to execute the read-out of many human genes and the genes of many other **eukaryotic** organisms, and eukaryotic host cells must be used. Animals that carry genetically engineered heritable genes are called transgenic. Transgenic animals have included lactating mammals such as sheep, goats, cows, and pigs. Most commonly an animal is engineered to produce a large quantity of a particular human protein in its milk. A widely used technique includes injecting a segment of DNA, human or animal, that contains the appropriate human gene (the DNA construct) into an embryo, and then implanting the embryo in a surrogate mother. If the technique is successful, the milk of the mature animal will contain active human protein in sufficient amounts to be of value. A herd of genetically engineered animals could then be produced using this technique, or possibly, eventually, via reproductive cloning.

Plant cells can also be used to mass-produce human proteins. Corn, soybean, and tobacco plants have been used in this way. The yield of protein from plants is generally higher than that from animals; however, human cells link carbohydrates to some antibodies, and these molecules cannot yet be produced in plants. Transgenic crops that are harvested for food are far more common than those used to produce human proteins.

Therapeutic cloning sometimes calls for the use of human stem cells. Stem cells are believed to be cells that have the potential to become any cell that exists in the mature organism; hence, it is felt that they might be used in the future to repair or even regenerate organs, such as the heart or pancreas, or portions of organs. Human stem cells were isolated in 1998. If a patient's stem cells were needed and were not available, cells from existing stem cell lines could be used, but in these cases, nuclear transfer would be required. This is presently legal in Britain but illegal in the United States. An alternative source would be generic stem cells combined with the administration to the patient of any necessary antirejection drugs. SEE ALSO GENES.

Vivienne A. Whitworth

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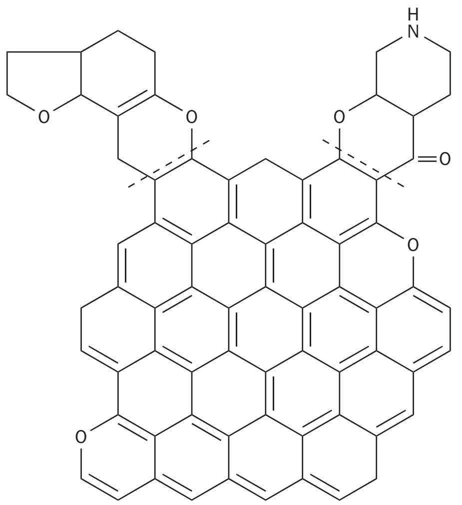
Coal

Coal, a naturally occurring combustible solid, is one of the world's most important and abundant energy sources. From its introduction 4,000 years ago as a fuel for heating and cooking, to its nineteenth- and twentieth-century use in generating electricity and as a chemical **feedstock**, coal, along with oil and natural gas, has remained an important source of energy. The United States alone has 1.7 trillion short tons of identified coal resources (natural deposits) and enough recoverable reserves (coal that can be developed for use) to meet its energy needs until the year 2225. Its demonstrated reserves include 274 billion short tons that existing technology can recover, representing 25 percent of the world's 1.08 trillion short tons of recoverable coal, and 508 billion short tons of coal that existing technology can potentially mine economically. Its recoverable reserves contain more than twice the energy of the Middle East's proven oil reserves. About 100 countries have recoverable reserves; 12 countries—among them Canada, the People's Republic of China, Russia, Poland, Australia, Great Britain, South Africa, Germany, India, Brazil, and Colombia—possess the largest reserves.

feedstock: raw materials necessary to carry out chemical reactions

Origin, Composition, and Structure of Coal

Geologists believe that underground coal deposits formed about 250–300 million years ago, when much of Earth was swamp covered with thick forest and plant growth. As the plants and trees died, they sank under Earth's wet surface, where insufficient oxygen slowed their decay and led to the formation of peat. New forests and plant life replaced the dead vegetation, and when the new forests and plants died, they also sank into the swampy ground. With the passage of time and accompanying heat buildup, underground lay-



$C_{70}H_{41}O_6N$

C = 84.76%
H = 4.14%
O = 9.68%
N = 1.42%

Figure 1. An example of the structure of coal.

ers of dead vegetation began to accumulate, becoming tightly packed and compressed, and gave rise to different kinds of coal, each with a different carbon concentration: anthracite, bituminous coal, subbituminous coal, and lignite. The English geologist William Hutton (1798–1860) reached this conclusion in 1833 when he found through microscopic examination that all varieties of coal contained plant cells and were of vegetable origin, differing only in the vegetation composing them. Because of its origin in ancient living matter, coal, like oil and gas, is known as a fossil fuel. It occurs in seams or veins in sedimentary rocks; formations vary in thickness, with those in underground mines 0.7–2.4 meters (2.5–8 feet) thick and those in surface mines, as in the western United States, sometimes 30.5 meters (100 feet) thick.

Until the twentieth century chemists knew very little about the composition and molecular structure of the different kinds of coal, and as late as the 1920s they still believed that coal consisted of carbon mixed with hydrogen-containing impurities. Their two methods of analyzing or separating coal into its components, destructive distillation (heating out of contact with air) and solvent extraction (reacting with different organic solvents such as tetralin), showed only that coal contained significant carbon, and smaller percentages of the elements hydrogen, oxygen, nitrogen, and sulfur. Inorganic compounds such as aluminum and silicon oxides constitute the ash. Distillation produced tar, water, and gases. Hydrogen was the chief component of the gases liberated, although ammonia, carbon monoxide and dioxide gases, benzene and other hydrocarbon vapors were present. (The composition of a bituminous coal by percentage is roughly: carbon [C], 75–90; hydrogen [H], 4.5–5.5; nitrogen [N], 1–1.5; sulfur [S], 1–2; oxygen [O], 5–20; ash, 2–10; and moisture, 1–10.) Beginning in 1910, research teams under the direction of Richard Wheeler at the Imperial College of Science and Technology in London, Friedrich Bergius (1884–1949) in Mannheim, and Franz Fischer (1877–1938) in Mülheim made important contributions that indicated the presence of benzenoid (benzenelike) compounds in coal. But confirmation of coal's benzenoid structure came only in 1925, as a result of the coal extraction and **oxidation** studies of William Bone (1890–1938) and his research team at Imperial College. The benzene tri-, tetra-, and other higher carboxylic acids they obtained as oxidation products indicated a preponderance of aromatic structures with three-, four-, and five-fused benzene rings, and other structures with a single benzene ring. The simplest structures consisted of eight or ten carbon atoms, the fused-ring structures contained fifteen or twenty carbon atoms.

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

Classification and Uses of Coal

European and American researchers in the nineteenth and early twentieth centuries proposed several coal classification systems. The earliest, published in Paris in 1837 by Henri-Victor Regnault (1810–1878), classifies types of coal according to their proximate analysis (determination of component substances, by percentage), that is, by their percentages of moisture, combustible matter, fixed carbon, and ash. It is still favored, in modified form, by many American coal scientists. Another widely adopted system, introduced in 1919 by the British scientist Marie Stopes (1880–1958), classifies types of coal according to their macroscopic constituents: clarain (ordinary bright coal), vitrain (glossy black coal), durain (dull rough coal), and fusain, also called mineral charcoal (soft powdery coal). Still another system is based on ultimate analysis (determination of component chemical elements, by percentage), classifying types of coal according to their percentages of fixed carbon, hydrogen, oxygen, and nitrogen, exclusive of dry ash and sulfur. (Regnault had also introduced ultimate analysis in his 1837 paper.) The British coal scientist Clarence A. Seyler developed this system in 1899–1900 and greatly expanded it to include large numbers of British and European coals. Finally, in 1929, with no universal classification system, a group of sixty American and Canadian coal scientists working under guidelines established by the American Standards Association (ASA) and the American Society for Testing Materials (ASTM) developed a classification that became the standard in 1936. It has remained unrevised since 1938.

The ASA–ASTM system established four coal classes or ranks—anthracite, bituminous, subbituminous, and lignite—based on fixed-carbon content and heating value measured in British thermal units per pound (Btu/lb). Anthracite, a hard black coal that burns with little flame and smoke, has the highest fixed-carbon content, 86–98 percent, and a heating value of 13,500–15,600 Btu/lb (equivalent to 14.2–16.5 million joules/lb [1 Btu=1,054.6 joules, the energy emitted by a burning wooden match]). It provides fuel for commercial and home heating, for electrical generation, and for the iron, steel, and other industries. Bituminous (low, medium, and high **volatile**) coal, a soft coal that produces smoke and ash when burned, has a 46–86 percent fixed-carbon content and a heating value of 11,000–15,000 Btu/lb (11.6–15.8 million joules/lb). It is the most abundant economically recoverable coal globally and the main fuel burned in steam turbine-powered electric generating plants. Some bituminous coals, known as metallurgical or coking coals, have properties that make them suitable for conversion to coke used in steelmaking. Subbituminous coal has a 46–60

volatile: low boiling, readily vaporized

Coal is one of the world's most abundant sources of energy.

percent fixed-carbon content and a heating value of 8,300–13,000 Btu/lb (8.8–13.7 million joules/lb). The fourth class, lignite, a soft brownish-black coal, also has a 46–60 percent fixed-carbon content, but the lowest heating value, 5,500–8,300 Btu/lb (5.8–8.8 million joules/lb). Electrical generation is the main use of both classes. In addition to producing heat and generating electricity, coal is an important source of raw materials for manufacturing. Its destructive distillation (carbonization) produces hydrocarbon gases and coal tar, from which chemists have synthesized drugs, dyes, plastics, solvents, and numerous other organic chemicals. High pressure coal hydrogenation or **liquefaction** and the indirect liquefaction of coal using Fischer–Tropsch syntheses are also potential sources of clean-burning liquid fuels and lubricants.

liquefaction: process of changing to a liquid form

Environmental Concerns

The major disadvantage of using coal as a fuel or raw material is its potential to pollute the environment in both production and consumption. This is the reason why many coal-producing countries, such as the United States, have long had laws that regulate coal mining and set minimum standards for both surface and underground mining. Coal production requires mining in either surface (strip) or underground mines. Surface mining leaves pits upon coal removal, and to prevent soil erosion and an unsightly environment, operators must reclaim the land, that is, fill in the pits and replant the soil. Acid mine water is the environmental problem associated with underground mining. Water that seeps into the mines, sometimes flooding them, and atmospheric oxygen react with pyrite (iron sulfide) in the coal, producing acid mine water. When pumped out of the mine and into nearby rivers, streams, or lakes, the mine water acidifies them. Neutralizing the mine water with lime and allowing it to settle, thus reducing the presence of iron pyrite before its release, controls the acid drainage.

combustion: burning, the reaction with oxygen

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

Coal **combustion** emits sulfur dioxide and nitrogen oxides, both of which cause **acid rain**. Several methods will remove or reduce the amount of sulfur present in many coals or prevent its release into the atmosphere. Washing the coal before combustion removes pyritic sulfur (sulfur combined with iron or other elements). Burning the coal in an advanced-design burner known as a fluidized bed combustor, in which limestone added to coal combines with sulfur in the combustion process, prevents sulfur dioxide from forming. Scrubbing the smoke released in the combustion removes the sulfur dioxide before it passes into the atmosphere. In a scrubber, spraying limestone and water into the smoke enables the limestone to absorb sulfur dioxide and remove it in the form of a wet sludge. Improved clean coal technologies inject dry limestone into the pipes leading from the plant's boiler and remove sulfur dioxide as a dry powder ($CaSO_3$) rather than a wet sludge. Scrubbing does not remove nitrogen oxides, but coal washing and fluidized bed combustors that operate at a lower temperature than older plant boilers reduce the amount of nitrogen oxides produced and hence the amount emitted.

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

Clean coal technologies and coal-to-liquid conversion processes have led to cleaner burning coals and synthetic liquid fuels, but acid rain remains a serious problem despite society's recognition of its damaging effects since 1852. Global warming resulting from the emission of the greenhouse gases, carbon dioxide, methane, and **chlorofluorocarbons**, is another coal combustion problem that industry and government have largely ignored since 1896, but it can no longer be avoided without serious long-term consequences.

Conclusion

Coal remains the world's most abundant fossil fuel, and along with petroleum and natural gas, it will continue to provide most of the world's energy. But all three are finite resources, and society should consume them wisely, not wastefully, in order to extend their lifetimes and reduce their harmful emissions. The conservation of fossil fuels and the development of alternative energies, such as solar and wind power, are pathways to a global society's cleaner energy future. SEE ALSO Fossil Fuels; Global Warming; Steel.

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Cobalt

27
Co
COBALT
58.933

MELTING POINT: 1,495°C
BOILING POINT: 2,870°C
DENSITY: 8.9 g/cm^3
MOST COMMON IONS: Co^{2+}, Co^{3+}

The name "cobalt" derives from the German word *Kobold*, meaning "mischievous spirit." Cobalt was first applied by sixteenth-century copper miners in the Hartz mountains of central Europe to gray metallic ores; this not only failed to produce copper when roasted, but also emitted dangerous fumes. It was found that the ores, after elimination of sulphur and **arsenic** by roasting, could be fused with sand to produce a blue glass called smalt. The source of the blue color, however, was not established until 1742, when Swedish chemist Georg Brandt isolated the previously unidentified **metal** cobalt.

arsenic: toxic element of the phosphorus group

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

Unlike its neighbors in the Periodic Table, iron, nickel, and copper, cobalt is not widespread in nature. It has an average abundance in Earth's crust of 25 parts per million (ppm); in ultrabasic rocks, where cobalt is most common, the average concentration is 110 ppm. Cobalt minerals may be concentrated by a range of geological processes to produce workable ores that typically contain 1,000–2,000 ppm.

Thirty-four cobalt minerals have been recognized, principally sulphides, selenides, arsenides, sulfarsenides, carbonates, sulfates, and arsenates. The main ore minerals are the sulfides linnaeite, carrolite, and cobaltiferous pyrite; the arsenides skutterudite and safflorite; the sulfosalt cobaltite; and the oxides asbolite (cobalt wad) and erythrite.

Cobalt has a wide range of industrial applications stemming from its variable **oxidation** states, color, and ability to form complexes. Its chief use, accounting for 45 percent of world demand, is in chemicals, particularly those used in catalysts, pigments, medical and agricultural agents, and nickel-cadmium (Ni-Cd) rechargeable batteries. Cobalt also has extensive metallurgical applications, including superalloys and other high temperature, erosion- and corrosion-resistant alloy steels. SEE ALSO MAGNETISM.

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

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Codon

The genetic **code** (which includes the codon) serves as a basis for establishing how genes encoded in **DNA** are decoded into proteins. A critical interaction in protein **synthesis** is the interaction between the codon in messenger **RNA** (mRNA) and the anticodon in an aminoacyl-transfer RNA (aminoacyl-tRNA).

code: mechanism to convey information on genes and genetic sequence

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

synthesis: combination of starting materials to form a desired product

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

A codon is a triplet of adjacent nucleotides in mRNA that specifies an amino acid to be incorporated in a protein. Because the codon can be made from three of the four possible ribonucleotides, there are 4^3 or 64 combinations, leading

The genetic information within a gene in DNA is encoded by a sequence of four nucleotides (A, T, G, and C). This must ultimately be translated into the twenty-letter (corresponding to amino acids) language of proteins. It is now known that this information is translated first into an **intermediate** message form called mRNA, and then converted into a specific protein. This latter process of converting from the "nucleotide alphabet" to the "protein alphabet" requires that specific segments on mRNA correspond to specific amino acids in the protein being manufactured. This connection is provided by the genetic code.

The translation process that occurs at the site of the **ribosomes** in the cytoplasm requires that the mRNA designate the codons that then specify the amino acid sequence for the protein. The codons on the mRNA must interact with the anticodons on the charged tRNA molecules, which bring to the site the specific amino acid residues. Watson-Crick complementary base pairing provides the specificity for this interaction.

to 64 different codons. The first letter of the codon is at the 5′-end, while the last letter is at the 3′-end. For example, 5′-AUG-3′.

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

ribosome: large complex of proteins used to convert amino acids into proteins

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

The **amino acid sequence** of a protein will be specified by the sequence of contiguous codons in the mRNA template. The initial codon in the mRNA establishes the reading frame and defines the protein's initial amino acid.

There are three types of codons. There is an initiation codon, AUG, which signifies the initial amino acid (and also codes for methionine residues in internal positions) in the protein. There are 61 codons, including AUG, that designate individual amino acids. The remaining three codons (UAA, UAG, and UGA) are termination codons (also called stop codons or nonsense codons), which do not code for amino acids, but signal the end of the mRNA message and provide the "stop" signal for protein synthesis.

Two amino acid residues, tryptophan and methionine, have unique codons—UGG and AUG, respectively. All other amino acids may be coded for by more than one codon, such that the code is said to be degenerate. This degeneracy is not uniform, but varies according to the particular amino acids. For example, three amino acids (arginine, leucine, and serine) have six codons, five amino acids have four, isoleucine has three, and nine amino acids have two. The first two letters of each codon provide the primary determinant in the specificity. For example, the codons for amino acid valine are GUU, GUC, GUA, and GUG. The open reading frame of the mRNA, which extends from the AUG codon to the termination codon, establishes the protein that is to be synthesized.

nuclear: having to do with the nucleus of a cell

The correspondence between codons and the amino acids that they specify appears to be nearly, but not quite, universal among species. This genetic code is identical within **nuclear** genes in all species examined, including *Escherichia coli*, viruses, various plants, and humans, with the exceptions being those genes that are encoded in mitochondria and genes found in a small number of other organisms. This is cited as evidence that all life-forms have a common evolutionary ancestor, with the genetic code being preserved throughout evolution. SEE ALSO Protein Synthesis; Protein Translation; Ribonucleic Acid.

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Coenzyme

Coenzymes are small organic molecules that link to enzymes and whose presence is essential to the activity of those enzymes. Coenzymes belong to the larger group called cofactors, which also includes **metal** ions; **cofactor** is the more general term for small molecules required for the activity of their associated enzymes. The relationship between these two terms is as follows

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

cofactor: inorganic component that combines with an apoenzyme to form a complete functioning enzyme

I. Cofactors
  A. Essential ions
    1. Loosely bound (forming metal-activated enzymes)
    2. Tightly bound (forming **metalloenzymes**
  B. Coenzymes
    1. Tightly bound prosthetic groups
    2 Loosely bound cosubstrates

metalloenzyme: a protein enzyme that contains at least one metal atom, often in an active site of the protein

Many coenzymes are derived from **vitamins**. Table 1 lists vitamins, the coenzymes derived from them, the type of reactions in which they participate, and the class of coenzyme.

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

Prosthetic groups are tightly bound to enzymes and participate in the **catalytic** cycles of enzymes. Like any **catalyst**, an enzyme–prosthetic group complex undergoes changes during the reaction, but before it can catalyze another reaction, it must return to its original state.

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

catalyst: substance that aids in a reaction while retaining its own chemical identity

Flavin **adenine** dinucleotide (FAD) is a prosthetic group that participates in several intracellular **oxidation**-reduction reactions. During the catalytic cycle of the enzyme succinate dehydrogenase, FAD accepts two electrons from succinate, yielding fumarate as a product. Because FAD is tightly bound to the enzyme, the reaction is sometimes shown this way

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

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

$$\text{succinate} + \text{E–FAD} \rightarrow \text{fumarate} + \text{E–FADH}_2$$

where E–FAD stands for the enzyme tightly bound to the FAD prosthetic group. In this reaction the coenzyme FAD is reduced to $FADH_2$ and remains tightly bound to the enzyme throughout. Before the enzyme can catalyze the oxidation of another succinate molecule, the two electrons now belonging to E–$FADH_2$ must be transferred to another electron acceptor, ubiquinone. The regenerated E–FAD complex can then oxidize another succinate molecule.

Cosubstrates are loosely bound coenzymes that are required in stoichiometric amounts by enzymes. The molecule nicotinamide adenine dinucleotide (NAD) acts as a cosubstrate in the oxidation-reduction reaction that is catalyzed by malate dehydrogenase, one of the enzymes of the citric acid cycle.

$$\text{malate} + \text{NAD}^+ \rightarrow \text{oxaloacetate} + \text{NADH}$$

Table 1. Vitamins, the coenzymes derived from them, the type of reactions in which they participate, and the type of coenzyme.

VITAMINS AND COENZYMES

Vitamin	Coenzyme	Reaction type	Coenzyme class
B_1 (Thiamine)	TPP	Oxidative decarboxylation	Prosthetic group
B_2 (Riboflavin)	FAD	Oxidation/Reduction	Prosthetic group
B_3 (Pantothenate)	CoA - Coenzyme A	Acyl group transfer	Cosubstrate
B_6 (Pyridoxine)	PLP	Transfer of groups to and from amino acids	Prosthetic group
B_{12} (Cobalamin)	5-deoxyadenosyl cobalamin	Intramolecular rearrangements	Prosthetic group
Niacin	NAD^+	Oxidation/Reduction	Cosubstrate
Folic acid	Tetrahydrofolate	One carbon group transfer	Prosthetic group
Biotin	Biotin	Carboxylation	Prosthetic group

SOURCE: Compiled from data contained in Horton, H. R., et al. (2002). *Principles of Biochemistry*, 3rd edition. Upper Saddle River, NJ: Prentice Hall.

In this reaction, malate and NAD^+ diffuse into the active site of malate dehydrogenase. Here NAD^+ accepts two electrons from malate; oxaloacetate and NADH then diffuse out of the active site. The reduced NADH must then be returned to its NAD^+ form. For each catalytic cycle, a "new" NAD^+ molecule is needed if the reaction is to occur; thus, stoichiometric quantities of the cosubstrate are needed. The reduced form of this coenzyme (NADH) is converted back to the oxidized form (NAD^+) via a number of simultaneously occurring processes in the cell, and the regenerated NAD^+ can then participate in another round of catalysis.

Coenzymes, then, are a type of cofactor. They are small organic molecules that bind tightly (prosthetic groups) or loosely (cosubstrates) to enzymes as they participate in catalysis. SEE ALSO Active Site; Cofactor; Enzymes.

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Cofactor

Enzymes are either proteins (polymers of amino acids) or ribozymes (polymers of ribonucleotides). Some protein-based enzymes require small molecules called cofactors to become fully functional. The relationship between enzymes and cofactors is shown by the equation

$$\textit{apoenzyme} + \textit{cofactor} = \textit{holoenzyme}$$

where **apoenzyme** refers to the nonfunctional protein and holoenzyme refers to the completely functional enzyme.

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

There are two types of cofactors: metal ions and small organic molecules. The latter of the two are also called coenzymes. The relationship between cofactor and coenzyme and some further subclassification can be seen in the following simple outline.

I. Cofactors
  A. Essential ions
    1. Loosely bound (metal-activated enzymes)
    2. Tightly bound (**metalloenzymes**)
  B. Coenzymes
    1. Tightly bound prosthetic groups
    2. Loosely bound cosubstrates

metalloenzyme: a protein enzyme that contains at least one metal atom, often in an active site of the protein

Metal-activated enzymes may have an absolute requirement for the metal ion, or they may simply have enhanced activity in the presence of the metal ion. Phosphofructokinase is an example of a metal-activated enzyme, which catalyzes the reaction

fructose-6-phosphate + ATP → fructose-1,6-bisphosphate + ADP

A divalent metal ion (Mg^{2+}) is needed to coordinate the phosphate groups on the ATP molecule in order for phosphofructokinase to successfully catalyze this reaction. Mg^{2+}, Mn^{2+}, Ca^{2+}, and K^+ often function as cofactors for metal-activated enzymes.

Metalloenzymes are enzymes that have a tightly bound metal ion. These metal ions are normally incorporated into the enzymes during enzyme **synthesis**, and removal of the metal ions often results in the complete denaturation of the enzyme. These metal ions may contribute either to the structure or the **catalytic** mechanism of a metalloenzyme. For example, horse liver alcohol dehydrogenase contains two tightly bound zinc ions (Zn^{2+}). The first zinc ion is structural: it is bound to four cysteine side chains and is essential to maintain the structural integrity of the enzyme. The second zinc ion is catalytic: it is bound to the side chains belonging to two cysteines and one histidine at the active site of the enzyme, and it participates in the catalytic cycle of the enzyme.

synthesis: combination of starting materials to form a desired product

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

A wide range of metal ions is present in metalloenzymes as cofactors. Copper zinc superoxide dismutase is a metalloenzyme that uses copper and zinc to help catalyze the conversion of superoxide **anion** to molecular oxygen and hydrogen peroxide. Thermolysin is a protease that uses a tightly bound zinc ion to activate a water atom, which then attacks a peptide bond. Aconitase is one of the enzymes of the citric acid cycle; it contains several iron atoms bound in the form of iron-sulfur clusters, which participate directly in the isomerization of citrate to isocitrate. Other metal ions found as cofactors in metalloenzymes include molybdenum (in nitrate reductase), selenium (in glutathione peroxidase), nickel (in urease), and vanadium (in fungal chloroperoxidase). SEE ALSO CATALYSIS AND CATALYSTS; COENZYMES; DENATURATION; ENZYMES; KREBS CYCLE.

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

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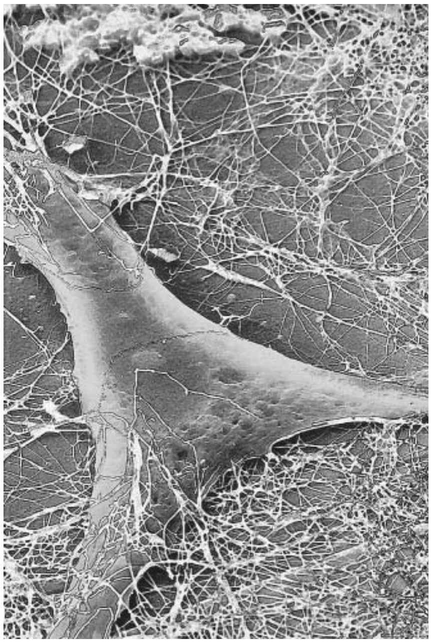
Coinage Metal ***See Copper, Gold, Nickel, Silver.***

Collagen

Collagen is a family of proteins; in animals these proteins play critical roles in tissue architecture, tissue strength, and cell to cell relationships. The major component of all connective tissue matrixes, collagen is found in tissues such as skin, blood vessels, bone, tendon, and ligament, and is characterized by tremendous strength.

The word "collagen" derives from the Greek word for "glue"; this derivation is based on the observation that insoluble collagen, when heated in water, becomes soluble, gummy gelatin that can be used in the manufacture of glues or as a thickener in foods. There are ten known forms of collagen that, because of differences in functional requirements and chemical environments, differ in some details of composition. All forms of collagen share the same basic structure: three **polypeptide** chains coiled together to form a triple **helix**. (These triple coils, in turn, become coiled together.) Collagen polypeptide chains generally contain around 1,000 amino acids.



A scanning electronic micrograph of a fibroblast and collages fibers. Collagen is a major component of connective tissue.

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

helix: form of a spiral or coil such as a corkscrew

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

cofactor: inorganic component that combines with an apoenzyme to form a complete functioning enzyme

tropocollagen: fibers, or fibrils, consisting of three polypeptide sequences arranged in a helix

superhelix: helical-shaped molecule synthesized by another helical-shaped molecule

fibril: slender fiber or filament

covalent bond: bond formed between two atoms that mutually share a pair of electrons

biosynthesis: the synthesis of a substance in a living system

An individual collagen polypeptide chain has a large number of repeating amino acid sequences, most often glycine–X–Y, where X is often proline and Y is often hydroxyproline. Lysine, in its pure form or modified to hydroxylysine, is also found in collagen. Both hydroxyproline and hydroxylysine are formed via the enzyme-catalyzed oxidations of the proline and lysine amino acid side chains, which occur after the collagen polypeptide has been synthesized. These enzymatic reactions require ascorbic acid (**vitamin** C) as a **cofactor**.

Individual collagen polypeptides form an extended, left-handed triple helix, which is longer and less compact than the α-helixes often seen in proteins. Three of these helixes then form a molecule of **tropocollagen**, the basic building block of collagen, by coiling around a central axis in a right-handed, triple-helical arrangement. The side chain of every third amino acid is very close to the central axis of this **superhelix**. Glycine, with the smallest side chain of any amino acid, is more easily accommodated in these arrangements than the larger, bulkier amino acids.

Tropocollagen molecules associate in a staggered fashion to form collagen **fibrils**, which are stronger than steel wire of similar size. Collagen fibrils are strengthened and stabilized mainly by covalent cross-links, existing both within and between individual tropocollagen molecules. These crosslinks represent the enzyme-catalyzed formation of **covalent bonds** involving lysine and hydroxylysine side chains. The extent of cross-linking depends on the specific function of the collagen molecule involved and the age of the animal; older animals have more highly cross-linked and therefore more rigid collagen.

There are a number of collagen-related disorders that have been identified. Many of these are the result of derangements in the **biosynthesis** of collagen. Scurvy, characterized by bleeding gums, loose teeth, skin lesions, and weakened blood vessels, results from severe vitamin C deficiency, which makes it almost impossible for afflicted individuals to form hydroxyproline and hydroxylysine. The conditions, known collectively as the Ehlers–Danlo syndromes, result from defects in the processing of collagen polypeptides.

In addition to its importance in the production of animal glue, collagen is the basis for gelatin, which forms when collagen fibers are denatured as a result of heating and then get tangled up with each other. Collagen is also used for various biomedical applications. SEE ALSO DENATURATION; PEPTIDE BOND; PROTEINS.

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Colligative Properties

Colligative properties are those properties of solutions that depend on the number of dissolved particles in solution, but not on the identities of the solutes. For example, the freezing point of salt water is lower than that of pure water, due to the presence of the salt dissolved in the water. To a good approximation, it does not matter whether the salt dissolved in water is sodium chloride or potassium nitrate; if the molar amounts of solute are the same and the number of ions are the same, the freezing points will be the same. For example, $AlCl_3$ and K_3PO_4 would exhibit essentially the same colligative properties, since each compound dissolves to produce four ions per formula unit. The four commonly studied colligative properties are freezing point depression, boiling point elevation, vapor pressure lowering, and osmotic pressure. Since these properties yield information on the number of solute particles in solution, one can use them to obtain the molecular weight of the solute.

Freezing Point Depression

The presence of a solute lowers the freezing point of a solution relative to that of the pure solvent. For example, pure water freezes at 0°C (32°F); if one dissolves 10 grams (0.35 ounces) of sodium chloride (table salt) in 100 grams (3.53 ounces) of water, the freezing point goes down to −5.9°C (21.4°F). If one uses sucrose (table sugar) instead of sodium chloride, 10 grams (0.35 ounces) in 100 grams (3.53 ounces) of water gives a solution with a freezing point of −0.56°C (31°F). The reason that the salt solution has a lower freezing point than the sugar solution is that there are more particles in 10 grams (0.35 ounces) of sodium chloride than in 10 grams (0.35 ounces) of sucrose. Since sucrose, $C_{12}H_{22}O_{11}$ has a molecular weight of 342.3 grams (12.1 ounces) per mole and sodium chloride has a molecular weight of 58.44 grams (2.06 ounces) per mole, 1 gram (0.035 ounces) of sodium chloride has almost six times as many sodium chloride units as there are sucrose units in a gram of sucrose. In addition, each sodium chloride unit comes apart into two ions (a sodium cation and a chloride **anion**) when

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

The freezing point depression of a solution containing a dissolved substance, such as salt dissolved in water, is a colligative property.

dissolved in water. Sucrose is a nonelectrolyte, which means that the solution contains whole $C_{12}H_{22}O_{11}$ molecules. In predicting the expected freezing point of a solution, one must consider not only the number of formula units present, but also the number of ions that result from each formula unit, in the case of ionic compounds. One can calculate the change in freezing point (ΔT_f) relative to the pure solvent using the equation:

$$\Delta T_f = i\, K_f\, m$$

where K_f is the freezing point depression constant for the solvent (1.86°C·kg/mol for water), m is the number of moles of solute in solution per kilogram of solvent, and i is the number of ions present per formula unit (e.g., $i = 2$ for NaCl). This formula is approximate, but it works well for low solute concentrations.

Because the presence of a solute lowers the freezing point, many communities put salt on their roads after a snowfall, to keep the melted snow from refreezing. Also, the antifreeze used in automobile heating and cooling systems is a solution of water and ethylene glycol (or propylene glycol); this solution has a lower freezing point than either pure water or pure ethylene glycol.

Boiling Point Elevation

The boiling point of a solution is higher than that of the pure solvent. Accordingly, the use of a solution, rather than a pure liquid, in antifreeze serves to keep the mixture from boiling in a hot automobile engine. As with freezing point depression, the effect depends on the number of solute particles present in a given amount of solvent, but not the identity of those particles. If 10 grams (0.35 ounces) of sodium chloride are dissolved in 100 grams (3.5 ounces) of water, the boiling point of the solution is 101.7°C (215.1°F; which is 1.7°C (3.1°F) higher than the boiling point of pure water). The formula used to calculate the change in boiling point (ΔT_b) relative to the pure solvent is similar to that used for freezing point depression:

$$\Delta T_b = i\,K_b\,m,$$

where K_b is the boiling point elevation constant for the solvent (0.52°C·kg/mol for water), and m and i have the same meanings as in the freezing point depression formula. Note that ΔT_b represents an increase in the boiling point, whereas ΔT_f represents a decrease in the freezing point. As with the freezing point depression formula, this one is most accurate at low solute concentrations.

Vapor Pressure Lowering

The vapor pressure of a liquid is the **equilibrium** pressure of gas molecules from that liquid (i.e., the results of evaporation) above the liquid itself. A glass of water placed in an open room will evaporate completely (and thus never reach equilibrium); however, if a cover is placed on the glass, the space above the liquid will eventually contain a constant amount of water vapor. How much water vapor is present depends on the temperature, but not on the amount of liquid that is present at equilibrium (provided some liquid is present at equilibrium). (At room temperature, the vapor pressure of pure water is about 20 Torr, which is about one-fortieth of the total atmospheric pressure on a "normal" day at sea level.)

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

If, instead of pure water, an **aqueous solution** is placed in the glass, the equilibrium pressure will be lower than it would be for pure water. Raoult's law states that the vapor pressure of the solvent over the solution is proportional to the fraction of solvent molecules in the solution; that is, if two-thirds of the molecules are solvent molecules, the vapor pressure due to the solvent is approximately two-thirds of what it would be for pure solvent at that temperature. If the solute has a vapor pressure of its own, then the total vapor pressure over the solution would be:

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

$$P_{\text{vap}} = \frac{2}{3}\,(\text{pure solvent vapor pressure}) + \frac{1}{3}\,(\text{pure solute vapor pressure})$$

Generally, one expects that solutes which are liquids in their pure form (such as ethyl alcohol) will have some vapor pressure of their own, whereas ionic compounds (such as sodium chloride) will not contribute to the total vapor pressure over the solution.

One consequence of this lowering in vapor pressure may be observed in a spilled can of soda. As the water evaporates, the soda becomes more sugar and less water, until the vapor pressure of the water is so low that it barely evaporates. As a result, the spilled soda remains sticky for a long time. Contrast this behavior with that of a water spill.

Osmotic Pressure

Osmosis is the process whereby a solvent passes through a semipermeable membrane from one solution to another (or from a pure solvent into a solution). A semipermeable membrane is a barrier through which some substances may pass (e.g., the solvent particles), and other species may not (e.g., the solute particles). Important examples of semipermeable membranes are the cell walls in cells of living things (plants and animals). Osmosis tends to drive solvent molecules through the semipermeable membrane from the low solute concentrations to the high solute concentrations; thus, a "complete"

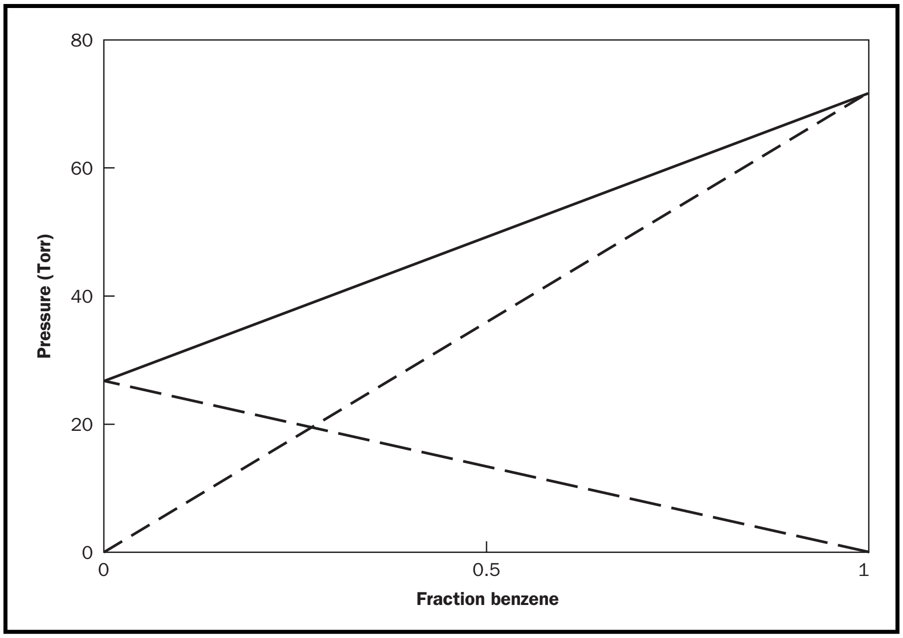

Figure 1. Vapor pressure over a benzene-toluene solution, plotted as a function of the fraction of benzene molecules in the solution. The solid curve is the total vapor pressure, while the short-dashed and long-dashed curves are the vapor pressures from the benzene and toluene, respectively. Note that the two dashed curves add up to the solid curve.

osmosis process would be one that ends with the solute concentrations being equal on both sides of the membrane. Osmotic pressure is the pressure that must be applied on the high concentration side to stop osmosis.

Osmosis is a very useful process. For example, meats can be preserved by turning them into jerky: The meat is soaked in a very concentrated salt solution, resulting in dehydration of the meat cells. Jerky does not spoil as quickly as fresh meat, since bacteria on the surface of the salty meat will fall victim to osmosis, and shrivel up and die. This process thus extends the life of the meat without the use of refrigeration.

There are times when one wishes to prevent osmosis when two solutions (or a pure solvent and a solution) are on opposite sides of a semipermeable membrane. Osmosis can be prevented by applying pressure to the more concentrated solution equal to the osmotic pressure on the less concentrated side. This can be accomplished either physically, by applying force to one side of the system, or chemically, by modifying a solute concentration so that the two solute concentrations are equal. (If one applies a pressure greater than the osmotic pressure to the higher concentration solution, one can force solvent molecules from the concentrated solution to the dilute solution, or pure solvent. This process, known as reverse osmosis, is often used to purify water.) A hospital patient receiving fluids intravenously receives an intravenous (IV) solution that is isotonic with (i.e., at the same solute concentration as) his or her cells. If the IV solution is too concentrated, osmosis will cause the cells to shrivel; too dilute a solution can cause the cells to burst. Similar problems would be experienced by freshwater fish swimming in salt water, or saltwater fish swimming in freshwater. The osmotic pressure, like other colligative properties, does not depend on the identity of the solute, but an electrolyte solute will contribute more particles per formula unit than a nonelectrolyte solute. **SEE ALSO** Solution Chemistry.

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Colloids

Somewhere between the sizes of an atom and a grain of sand lies the realm of small particles called colloids. As will become evident, they are everywhere. The simplest colloidal materials, also generally known as suspensions or dispersions, consist of two mixed phases. The continuous or dispersing **phase** may be gas, liquid, or solid (or even plasma, the fourth phase of matter). Air, water, and plastics are common examples. The colloid particles make up the dispersed or suspended phase when uniformly distributed in the second, continuous phase. The dispersed matter may also be gas, liquid, or solid, and any combination in more complex suspensions. Colloidal dispersions are considered **homogeneous** mixtures even though they can be **heterogeneous** at or below the microscale.

phase: homogeneous state of matter consisting of gases, liquids, or solids

homogeneous: relating to a uniform mixture of substances

heterogenous: relating to a mixture of diverse substances

Colloids are typically defined as having at least one linear dimension approximately between 1 nanometer (3.94 × 10^{-8} inches) and 1 micrometer, or micron (3.94 × 10^{-5} inches). A length-scale restriction for colloids is straightforward but arbitrary and misleading; there are no absolute bounds. It is best to think of a colloid in terms of how the material behaves with respect to inertial or body forces, such as gravity and fluid flow. For example, particles that do not quickly settle out or float to the top of their dispersed phase are considered colloidal. Wood fibers used in paper-making behave as colloids in water even though they can be tens of microns in diameter and many millimeters in length; individual fibers would not be considered colloidal in air where they would settle in seconds.

The scientific study of colloids began during the late 1800s with the continuing development of high-resolution microscopy and light-scattering theory (by Lord Rayleigh in 1871). Optical microscopy can view objects as small as approximately one-half the wavelength of light used, or roughly three-tenths of a micron for white light. Much smaller objects may still be located under the microscope by light scattering, but particle size becomes indistinguishable. Particle sizes can be measured to thousandths of a micron by carefully measuring the intensity of light scattered at different relative angles. Electron microscopy is capable of reproducing images at this scale, sometimes with atomic resolution.

Classification of Materials

Most kinds of colloidal suspensions maintain microscopic phase separation between two or more materials while having a uniform macroscopic distribution of each. Aerosols are fine liquid droplets or solid particulates that form in a gas phase. The inverse of an aerosol is a foam—gas bubbles or pockets trapped in a liquid or solid medium. Liquid foams often have neither a truly continuous phase nor a dispersed colloid in the usual sense. The bubbles are frequently very large with liquid films for separating them that are thin enough to exhibit colloidal characteristics. Soapsuds in a bathtub are a prime example of this phenomenon.

Aerosols of dust, smoke, mist, and fog are the most convenient colloids for observing light-scattering phenomena outside of the laboratory. This is demonstrated by the orange or red color of sunsets that results from dust and smoke blocking shorter wavelengths of light more than longer ones: violet, indigo, blue, and green over yellow, orange, and red. When the sun is higher, the light path through the atmosphere is much shorter with fewer dust particles to scatter it. Sunrise is not usually as red as sunset because

A nanometer (nm) is one-billionth of a meter (10^{-9} m, or 3.94×10^{-8} inches), approximately six water molecules end-to-end. A micron (μm) is 1,000 nanometers or one-thousandth of a millimeter (10^{-6} m, or 3.94×10^{-5} inches); the thickness of one strand of hair is typically 50–100 microns ($1.97–3.93 \times 10^{-3}$ inches) in diameter. Fog and clouds contain water droplets of smaller diameters but still above 1 micron. Red blood cells are about 7 microns (2.76×10^{-4} inches), smoke particles under a micron to 10 nanometers (3.94×10^{-5} inches to 3.94×10^{-7} inches). Very large molecules called polymers (e.g., **DNA**, cellulose, nylon) are also colloids and may be as large as tens of nanometers, comparable to viruses.

larger particles entrained in hotter, daytime air currents settle out in the calmer and cooler night atmosphere. Light scattering also explains why yellow or amber fog lights actually improve visibility in fog and higher-intensity headlights do not. Increasing intensity yields increased scattering, whereas eliminating shorter wavelengths reduces the effect.

Liquid drops dispersed in a second liquid medium are called emulsions and may be the most important of all colloids, including blood and milk. Solid colloids suspended in liquid are called sols, or hydrosols, when waterborne. Solid suspensions include ice cream, sedimentary rock formations, colored plastics and ceramics filled with pigment particles (as opposed to dyes), and other synthetic composites. Composites are made from two solids to form a hybrid material with the desirable properties of each constituent: for example, a plastic continuous phase for its light weight with a **metal** or ceramic filler for strength.

Colloidal suspensions of polymers and **surfactants** present two distinct groups compared to other dispersed or dissolved materials and will be discussed in more detail below.

Interfaces and Interparticle Forces

Surface area is more important than size for defining colloids. They behave differently than classic objects, or macroscopic bodies, because of their high surface-to-volume ratio, or more accurately, surface-to-mass. The force due to gravity acts on the mass while **intermolecular forces** effectively act at particle surfaces. If these interparticle or surface forces are large enough to alter the effects of gravity on an object, then it has the characteristics of a colloid. For example, gold is more than nineteen times as dense as water and should sink in it. But a nanometer-sized gold sphere (a few hundred atoms) has so little mass that the forces of water molecules hitting it from all directions are enough to make it effectively buoyant. This effect of thermal energy in a dispersing fluid is called **Brownian motion**. The colloidal gold may remain stable for many years as long as it never collides with another interface, that is, the boundary between phases. The concept behind the adage "like dissolves like" is as important for colloids as it is for solutions.

Atomic and molecular interactions determine both chemical solubility and colloidal stability. Similar molecules attract each other more than dissimilar ones. This universal **attraction** between everything, called London dispersion, is the result of electron motion. Dispersion forces are partly re-

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

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

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

intermolecular force: force that arises between molecules, generally it is at least one order of magnitude weaker than the chemical bonding force

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

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

The Scottish botanist Robert Brown (1773–1858), who also discovered the cell nucleus, first noticed small pollen particles wiggling and moving randomly under a microscope. Higher temperatures result in larger kinetic energies in the dispersant molecules, keeping even larger particles from sedimenting or floating. Thus, temperature is also a determining parameter in the definition of a colloid.

Light passing through a bottle containing sodium hydroxide (NaOH, left), and a bottle containing a colloidal mixture (right).

sponsible for keeping gold from dissolving in water since the two are not very similar. With this logic, a second gold particle in water would be attracted to the first and stick to it. This is called aggregation and cohesion; the aggregation of two unlike particles or interfaces is called adhesion.

More than London dispersion forces are often present. Even though a single molecule or atom has no **net charge**, it often has stable partial charges of equal positive and negative magnitudes, together called a dipole. Dipole interactions are attractive and often grouped with London dispersion under the collective label van der Waals interaction. Water is a highly polar molecule and gold is easily polarized, arguing for the even greater probability of aggregation. But as a metal, the gold interface with water easily builds up surface charge that repels other gold interfaces through the electrostatic or coulombic interaction. Nearly all materials acquire surface charge in water, more often negative than positive. Several other interparticle forces exist, but van der Waals and electrostatic forces usually determine colloidal behavior.

net charge: total overall charge

Surfactants, Adsorption, and Micelles

Molecules and surfaces are often qualitatively categorized as either **hydrophilic** (water-loving) or **hydrophobic** (water-fearing). Surface active agents or surfactants have both characteristics. One end of a simple surfactant is hydrophilic, the polar or ionic head group. The rest of the molecule is the hydrophobic tail, such as an oily hydrocarbon. Having very dissimilar parts in solution attracts the molecule to surfaces, as in detergency.

hydrophilic: a part of a molecule having an affinity for water

hydrophobic: a part of a molecule that repels water

Surfactants concentrate at interfaces by adsorption to remove lyophobic (solvent-fearing) parts from the solvent. This behavior lowers the liquid's surface tension; that is to say, it lessens the imbalance of intermolecular forces between the solvent and its surroundings. The surface tension of pure water causes it to bead up on hydrophobic surfaces, such as a water-proofed jacket or a rain-treated windshield. Liquids with lower surface tensions, such as oils and alcohols, bead up to lesser extents. Water can be made to wet hydrophobic material by adding surfactant; this is sometimes called "breaking" the surface tension.

At low concentrations, surfactants form traditional solutions. At higher concentrations, surfactant molecules may self-assemble into colloidal-scale structures in bulk solution referred to as micelles. They can be spheres, cylinders, **vesicles**, or bilayer sheets with nanometer to micron dimensions. Above the critical micelle concentration (CMC), micelles begin to grow by molecular association or aggregation. Hydrophobic tails escape water by sticking together in a core shielded by a shell of head groups. Surfactant solubility may sometimes be too low at room temperature for micellization; not enough molecules can dissolve to start associating.

vesicle: small compartment in a cell that contains a minimum of one lipid bilayer

Emulsions and Foams

Oil in vinegar (mostly water) for salad dressing is a common **emulsion**. However, this is not a stable colloidal system. Usually, salad dressings must be shaken vigorously to redisperse the oil before pouring. The kinetic energy of shaking breaks up the oil into small droplets. But the oil quickly separates again, aggregating into a large, hydrophobic phase. This is called coalescence for droplets since they not only attach but also merge into a single, larger drop. The interfacial tension between oil and water is very high; in other words, they do not mix easily. The acetic acid in vinegar can act as a surfactant, but a much better one is needed to reduce the oil—water interfacial tension enough for stable emulsion formation.

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

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

One surfactant crucial to life occurs naturally in the lung, without which babies could never take their first breaths in air. Pulmonary surfactant decreases the surface tension of liquid (mostly water) in the lungs to almost zero so that tiny air sacs called alveoli can expand to get oxygen into the blood. Water has very high surface tension due to strong molecular attractions, including polar and **hydrogen bonding**. Molten salts, mercury, and other liquid metals have much higher surface tensions, but nearly all liquids at room temperature have lower surface tensions than water.

Mayonnaise, on the other hand, is a relatively stable emulsion due mostly to high viscosity (more precisely, viscoelasticity), though surfactants are also present. The oil and water in mayonnaise cannot separate into phases because the emulsion droplets do not have enough energy for much movement. In less viscous emulsions, surfactants are responsible for stability. They reduce interfacial tension for the formation of small particles that either repel or very weakly attract each other. Brownian motion must be able to counter the effects of interparticle attraction, sedimentation, or creaming, which is floatation. Micellar suspensions could also be considered microemulsions, although this is debatable.

Stable foams may be formed by surfactant solutions. Thin liquid films separate gas bubbles, which can be colloidal but are usually much larger. Once formed, gravity eventually drains the liquid until the films break. Viscous additives can slow drainage and increase bubble lifetime significantly. Solid emulsions and foams are less common, the dispersing phase being solid while a liquid or gas phase is dispersed.

Solid Dispersions, Gels, and Polymer Solutions

"Colloid" comes from the Greek word meaning "glue," which was traditionally a sol. Nearly all paints are sols. Particles of pigment, binder, and

The silica-based mineral opal may be considered a solid emulsion when enough water is trapped to have microscopic domains larger than the usual hydration layer. A solid foam coffee cup, thermos, or packing filler is made from polymer expanded with microscopic air pockets. Porous polymer and ceramic membranes could also be viewed as solid foams. Ice cream is a more complicated colloid and may be considered both solid foam and solid suspension. It has at least three phases: ice crystals, air bubbles, and frozen fatty cream. Higher-quality ice cream has more finely dispersed phases for a smoother taste.

filler create the color, strength, and substance of the solid coating after drying. Most paints must be shaken to disperse the particles evenly before application. Many polishing compounds are highly concentrated sols, perhaps even a paste. Rather than separating, these may set over time; the solid particles aggregate. If they pack loosely, the solid network can trap solvent to form a sol-gel. Stirring may redisperse the particles into a sol state again. Silica is known to form gels and gel layers in water.

Polymers, or macromolecules, in solution are lyophilic colloids, implying that they dissolve. However, polymer can still be separated from solvent by physical means, unlike traditional solutions. This is a further implication of its colloidal status. Larger molecules may be filtered or centrifuged from small ones, although some solvent inevitably remains. Even here the physical separation criterion for solutions is not absolute, since zeolites can filter dissolved molecules by size exclusion to tenths of nanometers and atomic **isotopes** may be separated by centrifugation.

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

Polymers can also form gels, such as gelatin, as a solid suspension. Entangled polymer chains trap solvent. Some polymer mixtures form solid-in-solid solutions, such as poly(ethylene) and poly(propylene) blends in clothing fabrics. Polymers can also be surfactants, such as starch with hydrophilic and hydrophobic segments.

Colloids are extremely important to both commerce and life. The Information Age of the late twentieth century nurtured many advancements allowing more detailed investigation of colloidal materials. Lasers and computers, of course, have greatly affected all areas of science. In return, colloids play a major role in the semiconductor industry. Silica–alumina sols polish silicon wafers that go into diode lasers, memory chips, and microprocessors. Everyone takes advantage of colloidal suspensions, especially since the human body contains so many with its cells, proteins, and DNA. As society pushes to make so many things smaller, more functional, and more efficient, colloid science will become increasingly pertinent to technological developments. SEE ALSO Solution Chemistry.

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Nanotechnology is the interdisciplinary field that has evolved from the study of colloids and the techniques of integrated circuit fabrication. Biotechnology and the biological sciences are replete with numerous colloidal systems, including cells, cell membranes, viruses, bacteria, proteins, and DNA. Most of the hype in nanotechnology has centered on the future creation of microelectromechanical (MEM) devices and even nanobots. All endeavors in nanotechnology must deal with fundamental issues common to colloids, interparticle forces most directly. All areas of science are involved in nanotechnology, and it even began to have an impact on disciplines like business, economics, and law by the end of the twentieth century.

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Colorants *See Dyes, Pigments.*

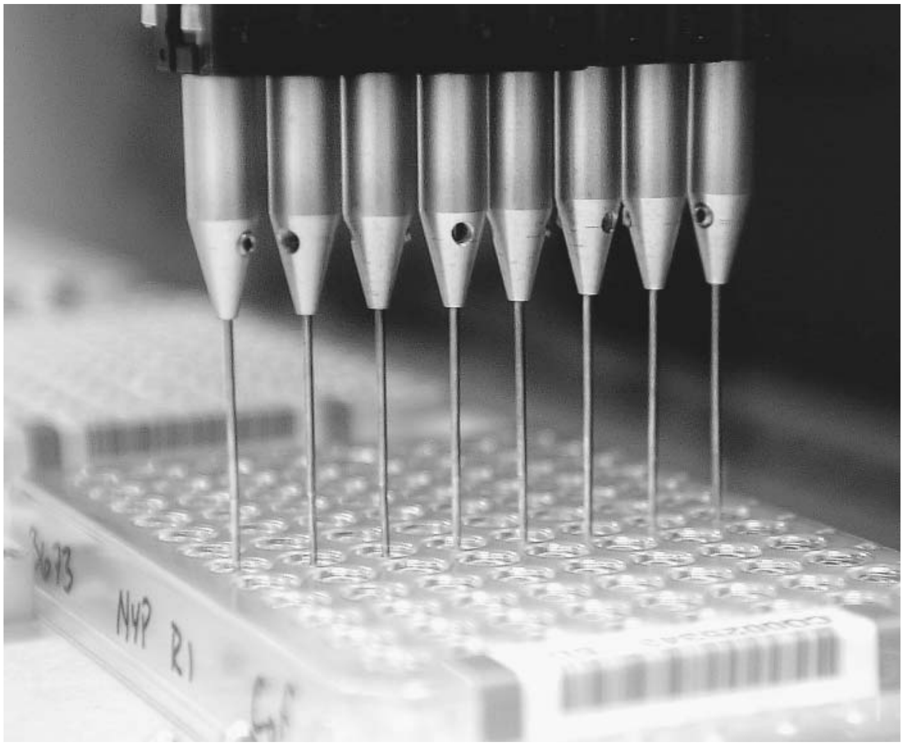
Combinatorial Chemistry

screen: process of comparing multiple reagents simultaneously to provide information on reaction of one reagent with another

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

Combinatorial chemistry is a sophisticated set of techniques used to synthesize, purify, analyze, and **screen** large numbers of chemical compounds, far faster and cheaper than was previously possible. The direct precursor of combinatorial chemistry was the solid-phase synthesis of **polypeptides** developed by American biochemist Robert Bruce Merrifield in the 1960s, followed by the advances in laboratory automation since then. Initial development of the field has been led by the pharmaceutical industry in the search for new drugs, but its applications are spreading into other fields of chemistry. Other terms associated with this field are *parallel array synthesis* and *high-throughput chemistry*.

Whereas classical synthetic chemistry involves the stepwise synthesis and purification of a single compound at a time, combinatorial chemistry makes it possible to synthesize thousands of different molecules in a relatively short amount of time, usually without the intermediate separation of compounds involved in the synthetic pathway, and with a high degree of automation. Such procedures result in the production of new compounds faster and in greater numbers than is possible with standard synthetic methods. The first and still the most common type of combinatorial synthesis involves attaching a molecular species onto a macroscopic substrate such as a plastic bead and performing one or several well-characterized chemical reactions on the species. After each reaction, the product mixture can be split among several reaction containers and then recombined after the reaction (a procedure called *mix and split*), or else carried out in parallel containers. The resulting mixture of compounds is referred to as a *molecular library* and can contain many thousands of individual compounds. The analysis, or *screening*, of these libraries to identify the compounds of interest, along with their subsequent isolation and identification, can be completed by a variety of methods. One example is *iterative deconvolution*; it involves the successive identification of each of the units backward along the chain of synthesized units. Another, called *positional scanning*, requires the multiple synthesis of a library, each time varying the location of a known unit along the chain and comparing the activities of the resulting libraries. More recent advances in library screening involve the "tagging" of a substrate with tiny radio frequency transmitters or unique two-dimensional barcodes. Another important recent advance by researchers allows combinatorial syntheses to be carried out in solution, which further extends the scope and utility of this field.



In a laboratory at Myriad Genetics, Salt Lake City, Utah, a robot adds solution to and stirs DNA samples from victims of the 2001 terrorist attack on New York City.

Although the initial applications of combinatorial and high-throughput chemistry have occurred in the pharmaceutical field, the same techniques are now being used successfully to aid in the discovery of new catalysts, polymers, and high temperature superconductors. SEE ALSO Chemical Informatics.

Bartow Culp

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Computational Chemistry

In 1929, shortly after the emergence of quantum mechanics, Paul Dirac made his famous statement that in principle the physical laws necessary to understand all of chemistry were at that point known—the only difficulty was that their application to chemical systems generally led to equations that were too difficult to solve. Consequently, at that time quantum principles could be rigorously applied only to simple atoms and molecules, such as H, He, H_2^+, and H_2.

During the 1930s the first approximate **quantum mechanical** methods for molecules were developed, leading to some success in modeling electronic behavior in many-electron molecules. For example, Eric Hückel developed a rudimentary molecular orbital model for the behavior of electrons in organic polyenes. During the late 1930s and early 1940s the first electronic digital computers were developed, and after World War II their use

quantum mechanical: theoretical model to describe atoms and molecules by wave functions significantly expanded the application of classical and quantum mechanical principles to chemical problems.

A measure of the progress that computer technology spawned was the awarding of the Nobel Prize in chemistry in 1966 to Robert Mulliken for his creation of molecular orbital theory and its use in the calculation of the electronic structure of molecules. In his acceptance speech Mulliken announced the emergence of computational chemistry as a recognized specialty within the field of chemistry: "In conclusion, I would like to emphasize strongly my belief that the era of computing chemists, when hundreds if not thousands of chemists will go to the computing machine instead of the laboratory for increasingly many facets of chemical information, is already at hand."

density-functional theory: quantum mechanical method to determine ground states

The 1998 Nobel Prize in chemistry, awarded to Walter Kohn (who developed the **density-functional theory**) and John Pople (who developed the use of computational methods in quantum chemistry) for their contributions to the advancement of computational chemistry, provided further evidence that the field had become a mature, reliable, and essential method of scientific inquiry. Today a vast literature exists, and computational chemistry has become an essential subject in the education of chemists at both the graduate and undergraduate levels.

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

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

The technical breadth of computational chemistry and the interdisciplinary character of its applications make the formulation of a concise definition challenging. Computational chemistry might be broadly defined as the attempt to model chemical and biochemical phenomena (structure, properties, reactivity, etc.) via computer-implementation of the theoretical principles of classical and quantum mechanical physics. Chemists and biochemists are interested in a wide array of molecules, including simple inorganic molecules, organic species of intermediate complexity, **transition metal** complexes with **heavy metal** ions, polymers, and biological macromolecules, such as proteins and nucleic acids. In their studies of these diverse species they have a wide range of computational tools at their command. Therefore, assessing the strengths and weaknesses of these tools, and choosing the most appropriate method for the task at hand is a serious challenge for the computational chemist.

Computational Quantum Chemistry

valence: combining capacity

At the most fundamental level chemical phenomena are determined by the behaviors of **valence** electrons, which in turn are governed by the laws of quantum mechanics. Thus, a "first principles" or *ab initio* approach to chemistry would require solving Schrödinger's equation for the chemical system under study. Unfortunately, Schrödinger's equation cannot be solved exactly for molecules or multielectron atoms, so it became necessary to develop a variety of mathematical methods that made approximate computer solutions of the equation possible.

nuclear: having to do with the nucleus of an atom

The Hartree–Fock (HF) approximation. The HF method is based on the Born–Oppenheimer and orbital approximations. Under the Born–Oppenheimer approximation the **nuclear** and electronic degrees of freedom of a molecule are decoupled, and the nuclei are held fixed while the electronic contribution to the energy is calculated. In the orbital approximation

British chemist John A. Pople, co-recipient of the 1998 Nobel Prize in chemistry, "for his development of computational methods in quantum chemistry."

the electrons occupy individual spin-orbitals, and as a consequence the *N*-electron Schrödinger equation is transformed into *N* one-electron equations. Both approximations facilitate computation, and the HF method proceeds by selecting a trial wave function (a molecular orbital formed as a linear combination of **atomic orbitals**, LCAO-MO) containing adjustable parameters, and subsequently solving a set of *N* coupled **integro-differential** equations through an iterative (self-consistent field) procedure.

Post-Hartree–Fock (PHF) methods. HF calculations for small to intermediate sized molecules generally yield reliable geometries, but fail to various degrees in predicting other important molecular properties. This is due to the **electron correlation error** introduced by the orbital approximation. PHF implementations introduce electron correlation into the calculation either by Møller–Plesset perturbation methods (MP2 and MP4), or by using wave functions based on many electron configurations (configuration interaction), rather than the **single Slater determinant** wave functions used in the HF method. These methods yield excellent results, but are computationally expensive (and good quantitative agreement with experiment comes at a price). As the level of theoretical rigor increases, the ability to interpret

atomic orbital: mathematical description of the probability of finding an electron around an atom

integro-differential: complex mathematical model used to calculate a phase transition

electron correlation error: quantum mechanical method for studying atoms, ions, or molecules

single Slater determinant: wave function used to describe atoms and molecules the results in terms of traditional chemical concepts decreases. For this reason, many chemists are willing to sacrifice quantitative agreement for qualitative, conceptual understanding.

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

Semiempirical quantum mechanics. The computational effort in *ab initio* calculations increases as the fourth power of the **size of the basis set**, and, therefore, its application to large molecules is expensive in terms of time and computer resources. Consequently, semiempirical methods treating only the valence electrons, in which some integrals are ignored or replaced by empirically based parameters, have been developed. The various semiempirical parameterizations now in use (MNDO, AM1, PM3, etc.) have greatly increased the molecular size that is accessible to quantitative modeling methods and also the accuracy of the results.

Density functional theory (DFT). DFT is an alternative to the HF method, in which the fundamental role is played by the electron density ψ^2, rather than the wave function. The basis for this method is a proof by Pierre Hohenberg and Kohn that all physical properties of a molecule are completely determined by its electron density. The computational savings that DFT offers come from the fact that the wave function of an *n*-electron molecule depends on 3*n* spatial coordinates, whereas the electron density depends on just three spatial coordinates. Consequently, DFT calculations generally scale as the third power of the size of the basis set, rather than the fourth power of the HF methods.

Classical Computational Methods

Many chemical and biochemical systems of interest are too large for analysis with quantum mechanical methods, either *ab initio* or semiempirical. However, some of their properties may be modeled by classical or semiclassical methods. Classical computational methods do not provide electronic structure information.

Molecular mechanics (MM). MM is a nonquantum mechanical method of computing molecular structures and properties that treats a molecule as a flexible collection of atoms held together by chemical bonds. The method minimizes the molecular potential energy, which is generally calculated classically in terms of internal degrees of freedom such as bond lengths, bond angles, dihedral angles, and electrostatic and van der Waals nonbonding interactions. The MM minimization depends on an empirically-based parameterization scheme and is able to handle molecules with thousands of atoms. The MM method has been highly developed, especially by researchers in the pharmaceutical industry.

Molecular dynamics (MD). Within the MD method of computation, atomic and molecular trajectories are generated by the numerical integration of Newton's laws of motion. This requires specification of initial conditions and a knowledge of the forces acting on all constituents, which can be obtained either algebraically or numerically from a previously calculated potential energy surface. MD has important application in a variety of chemical disciplines, but is especially useful in biochemistry in the study of protein-folding, in probing alternative minimal energy states of macromolecules, and in other areas, such as enzyme-substrate docking.

Monte Carlo simulations (MC). MC computational methods are used to solve a wide variety of problems in mathematics and the natural sciences, including the evaluation of integrals, the solution of differential equations, and the modeling of physical phenomena. Unlike MD, which is **deterministic**, MC (as its name suggests) is based on the generation of random changes in the variables of a system, followed by reliance on some criterion for deciding whether the changes lead to a valid or significant new state of the system. For example, MC can be used to calculate bulk thermodynamic quantities by generating random changes in the positions of the atoms in an ensemble of molecules. The energy of the new arrangement is then calculated and its importance evaluated using the Boltzmann factor, ê(-E/kT). If this new arrangement passes the test, it is included (properly weighted, statistically) in the **manifold of ensemble states** that are used to calculate the average thermodynamic properties of the system being modeled.

deterministic: related to the assumption that all events are based on natural laws

manifold of ensemble states: a set of quantum states that meet the specific requirements (such as total energy) being considered in a calculation

Quantum mechanics/molecular mechanics hybrid method (QM/MM). MM is applicable to macromolecules such as enzymes, but cannot model the bond-breaking and bond-making that occurs within enzyme-substrate complexes at active sites. The solution is provided by a QM/MM hybrid approach, in which QM is used to model the active site and MM models are used for the rest of the enzyme structure.

Advances in computer technology and improved algorithm efficiency have greatly increased the size and range of chemical systems to which these computational methodologies can be applied. In addition, the increased availability of commercial software with efficient user interfaces for preparing input and analyzing output has made computational methods accessible to a rapidly growing number of chemists. SEE ALSO MOLECULAR ORBITAL THEORY; QUANTUM CHEMISTRY; THEORETICAL CHEMISTRY.

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Computer Chips ***See Semiconductors.***

Concentration Gradient

A concentration gradient occurs where the concentration of something changes over a certain distance. For example, a few drops of food dye in a glass of water diffuse along the concentration gradient, from where the dye exists in its highest concentration (for instance, the brightest blue or red) to where it occurs in its lowest concentration (the water is still clear). The diffusion will continue until the concentration of the dye becomes uniform in all directions of the water. Concentration gradients are the chemical driving force behind many processes that take place near cell membranes.

In general, two types of diffusion are found in living cells: passive and active. It is, however, very rare to encounter pure **passive diffusion**, where molecules or ions move freely across the cell membrane, following a concentration gradient. For example, water is free to move across a membrane in either direction. But if the solutes inside the cell are barred from moving across the membrane, the resulting phenomenon is called osmosis. The water passes across the membrane into a region of higher solute concentration attempting to reach the ideal **equilibrium**, where for each side of the membrane the water concentration is the same. This movement leads to the buildup of osmotic pressure, however, so the flow of water stops before the membrane bursts.

passive diffusion: mechanism of transporting chemical species across membranes

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

Active diffusion occurs when membranes translocate or move molecules or ions from regions of low concentration to those of higher concentration. For example, many cells are able to increase the internal concentration of solutes until very high levels are reached and considerable concentration gradients are established. In this case, a process other than diffusion must be available to supply the energy. Generally, the energy comes from the hydrolysis of **adenosine triphosphate (ATP)**, an energy-rich molecule. Active transport is very important for tissues that are specialized, such as nerve and muscle tissues as well as secretory (or excretory) tissues like the kidneys of animals and the gills of marine life, so solutes may be absorbed against concentration gradients.

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

In addition, ion concentration gradients existing between two sides of a membrane produce an electrical potential difference, ranging between 50 and 100 millivolts or mV (10^{-3} volt), the outside being positive with respect to the interior. This is the direct consequence of the distribution of cations, especially potassium and sodium ions. Any stimulation by electrical, mechanical, or chemical means at one point of the membrane will create a change in the potential membrane at that point. The altered potential, also called the active potential, will move as a wave over the membrane surface. This provides a means of rapid communication between different regions of a cell. In the case of an elongated nerve cell, this constitutes a nerve impulse.

It is interesting to note that this active potential is used by some fish, such as catfish and eel, to defend themselves as well as to stun their prey. The excitable membranes of the fish each develop a potential of 100 millivolts, but are stacked in such a manner that their potential differences add up to several hundred volts. SEE ALSO HYDROLYSIS; MEMBRANE; PROTEINS; TRANSMEMBRANE PROTEIN.

Joseph Bariyanga

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Coordination Compounds

Transition metals readily react with **halogens** to form binary compounds of various colors, for example: green-black **ferric** chloride ($FeCl_3$), deep blue cobalt chloride ($CoCl_2$), and golden yellow nickel bromide ($NiBr_2$). These compounds dissolve in water to give brightly colored solutions—but of *changed* colors: yellow solutions (containing Fe^{3+} ions), red solutions (Co^{2+} ions), and green solutions (Ni^{2+} ions). By evaporating the solutions, crystals of these new compounds can be obtained: yellow $FeCl_3 \cdot 6H_2O$, red $CoCl_2 \cdot 6H_2O$, and green $NiBr_2 \cdot 6H_2O$. Addition of ammonia to a green nickel solution changes its color to violet, and the compound $NiBr_2 \cdot 6NH_3$ can be crystallized. In all cases these beautiful color changes occur because a new chemical species has formed, and there have been changes in the bonding of the nonmetallic substance to the **metal** ion. Probably the best-known example of vivid color change is the dissolving of anhydrous white cupric sulfate ($CuSO_4$) in water to give a blue solution, containing $[Cu(H_2O)_4]^{2+}$. Addition of ammonia yields the deep blue $[Cu(NH_3)_4]^{2+}$, which forms crystals that have the formula $[Cu(NH_3)_4]SO_4 \cdot H_2O$.

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

halogen: element in the periodic family numbered VIIA (or 17 in the modern nomenclature) that includes fluorine, chlorine, bromine, iodine, and astatine

ferric: older name for iron in the +3 oxidation state

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

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

The neutral molecules NH_3 and H_2O bond directly to a metal atom by donating a lone pair of electrons to any empty orbital on the metal atom. **Anions** as well as neutral molecules can bond to a metal atom in this way. These neutral molecules or anions that bond to the metal are called **ligands**. Further examples of ligands are: Br^-, NO_2^-, CO, pyridine, $P(CH_3)_3$, and $O{=}As(C_2H_5)_3$. Some ligands can donate two pairs of electrons and are termed *bidentate*, for example, $H_2N–CH_2–CH_2–NH_2$ (ethylenediamine or en), and $O_2C–CO_2^{2-}$ (oxalate anion or ox).

ligand: molecule or ion capable of donating one or more electron pairs to a Lewis acid

A coordination compound (or coordination complex) consists of a **metal cation** or neutral atom to which neutral or negatively charged ligands have bonded. The number of ligand atoms to which the metal center is directly bonded is the metal cation's coordination number (c.n.), and this number is always greater than the regular **valence** or **oxidation** number (o.n.) of the metal. The coordination complex can be negatively charged, for example, $[AuCl_4]^-$, $[PtCl_6]^{2-}$, $[Co(NO_2)_6]^{3-}$, and $[Fe(CN)_6]^{3-}$; neutral, for example, $[Fe(CO)_5]$, $[Ni(PF_3)_4]$, and $[Rh(NH_3)_3Cl_3]$; or positively charged, for example, $[Cu(NH_3)_4]^{2+}$, $[Mn(H_2O)_6]^{2+}$, and $[Pt(NH_3)_5Cl]^{3+}$. $TiCl_4$ and UF_6 are neutral molecules (in which o.n. = c.n.), they are not coordination compounds; whereas $[AlCl_4]^-$ and $[FeF_6]^{3-}$ are coordination complexes in which the coordination number exceeds the oxidation number. The chromate anion, CrO_4, is not a coordination complex; the o.n. of the Cr atom is 6, but only four O atoms are bonded to it.

metal cation: positively charged ion resulting from the loss of one or more valence electrons

valence: combining capacity

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

Historical Development

By the mid-1870s Sophus Jørgensen in Denmark had systematized the synthetic methods for preparing the coordination compounds that were known at that time, especially those of cobalt(III). Only in 1893 was the mode of bonding in the complexes established, by Alfred Werner (who was awarded the Nobel Prize in 1913 for this work). Werner concluded that most coordination complexes were essentially **octahedral**, with six ligands bonded to a central metal ion (more or less, one above, one below, and four in the same plane as the metal ion). He deduced that Pd(II) and Pt(II) complexes were

octahedral: relating to a geometric arrangement of six ligands equally distributed around a Lewis acid; literally, eight faces

Table 1.

NAMING COORDINATION COMPOUNDS BASED ON COLOR

Color	Formula	Name
Yellow	$CoCl_3 \cdot 6NH_3$	Luteocobaltic chloride
Purple	$CoCl_3 \cdot 5NH_3$	Purpurocobaltic chloride
Green	$CoCl_3 \cdot 4NH_3$	Praseocobaltic chloride

square-planar, with four ligands bonded to the metal atom. He used the German word *Nebenvalenz* (meaning secondary valence) for coordination number, and *Hauptvalenz* (principal valence) for the oxidation number of the metal.

Nomenclature

Naming the compounds was originally based on color. The compound of empirical formula $[PtCl_2(NH_3)_2]$, now known to be $[Pt(NH_3)_4][PtCl_4]$, was named Magnus's green salt after its discoverer, Heinrich Gustav Magnus. The modern system, established by the International Union of Pure and Applied Chemistry (IUPAC), assigns names to compounds based on the identity of the metal, its oxidation state, the number and type of ligand (or ligands) attached to it, and the identities of the other cations and anions present. Some examples of IUPAC names are

$[Pt(NH_3)_2Cl_2]$	diamminedichloroplatinum(II)
$[Co(NH_3)_5Cl]Cl_2$	penta-amminecobalt(III) chloride
$K_4[Fe(CN)_6]$	potassium hexacyanoferrate(II)

The problem of nomenclature quickly becomes very great if, for example, a complex contains two different metal atoms linked by bridging groups.

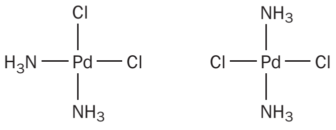
Stereoisomerism

As there is usually more than one way of arranging two or more ligands about a central metal ion, structural **isomers**, that is, two complexes of the same formula but different chemical and physical properties, are possible.

isomer: molecules with identical compositions but different structural formulas

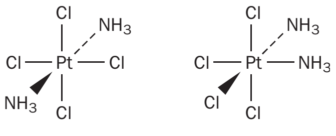
planar complex: arrangement of atoms in which all atoms lie within a common two-dimensional plane

Geometric isomers. Square-**planar complexes** [general formula MX_2B_2] and octahedral complexes [general formula MX_2B_4] can exist as geometric isomers, for example, *cis* and *trans* $[Pd(NH_3)_2Cl_2]$



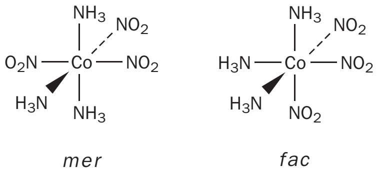
cis *trans*

and *cis* and *trans* $[Pt(NH_3)_2Cl_4]$.

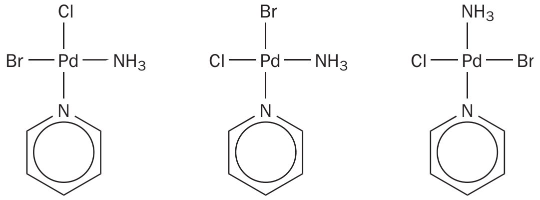


trans *cis*

In the case of octahedral complexes, [general formula MX_3B_3,] two isomers exist, *facial* (*fac*) and *meridional* (*mer*), for example, *fac* and *mer* $[Co(NH_3)_3(NO_2)_3]$.



A square-planar complex of formula [MABXY] has three isomers. An example is $[PdClBrNH_3py]$, whose isomers were prepared by the Russian chemist I. Chernyaev in 1926.



Three isomers of $[PdClBrNH_3py]$

Polymerization isomers. In the case of octahedral complexes, formula $[MX_xB_b]_n$, polymerization isomers are often possible. The value of n is greater than or equal to 1. Several compounds of empirical formula $[Co(NH_3)_3(NO_2)_3]$ can be isolated.

$[Co(NH_3)_3(NO_2)_3]^\circ$ ($n=1$)

$[Co(NH_3)_4(NO_2)_2]^+[Co(NH_3)_2(NO_2)_4]^-$ ($n=2$)

$[Co(NH_3)_6]^{3+}[Co(NO_2)_6]^{3-}$ ($n=2$)

There are several more possibilities.

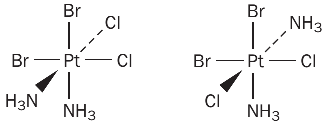
Hydration isomers. Hydration isomers exist for crystals of complexes containing water molecules, for example $CrCl_3z6H_2O$. This compound can exist in three different crystalline forms, in which the number of water molecules directly attached to the Cr^{3+} ion differs.

$[Cr(H_2O)_4Cl_2]Cl \cdot 2H_2O$	dark green
$[Cr(H_2O)_5Cl]Cl_2 \cdot H_2O$	light green
$[Cr(H_2O)_6]Cl_3$	gray-blue

In each case, the coordination number of the chromium cation is 6.

Optical isomers. Optical isomers exist for octahedral complexes that do not possess a center of inversion or a mirror plane of symmetry. The complex and its mirror image are not superimposable. One isomer will rotate the plane of polarized light to the left, the other will rotate polarized light to the right. The complexes are said to be chiral and **optically active**. Some examples are $[Co(ox)_3]^{3-}$; *cis* $[Rh(en)_2Cl_2]^+$; and *cis*, *cis*, *cis* $[PtCl_2Br_2(NH_3)_2]$.

optically active: capable of rotating the plane of plane-polarized light



Chiral pairs

monodentate: capable of donating one electron pair; literally, one-toothed

Each of the isomers will react at the same rate with simple **monodentate** ligands such as water. They differ only in their reactivity toward other chiral compounds and toward polarized light.

Stereochemistry

In addition to the common octahedral and square-planar complexes, several other types of complexes (which can be classified according to coordination number) are observed.

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

Coordination number 2: collinear. Collinear complexes are common in the case of **heavy metal** cations of d^{10} electron configuration. Examples of collinear complexes are $[Au(CN)_2]^-$, formed during the extraction of gold from its ore, and $[Ag(NH_3)_2]^+$, formed when AgCl dissolves in ammonia solution.

Coordination number 3: trigonal planar. Trigonal-planar geometry is quite rare; these complexes are found in instances in which ligands are large and steric repulsions are dominant, for example, $[Pt\{P(phenyl)_3\}_3]$.

Coordination number 4: tetrahedral. Tetrahedral complexes are common for d^{10} metal ion species such as Zn^{2+} and Ga^{3+}, and d^7 species, such as Co^{2+}. Examples of tetrahedral complexes are $[ZnCl_2(pyridine)_2]$; $[GaCl_4]^-$; and $[CoCl_2(4\text{–}methylpyridine)_2]$, which is deep blue.

Coordination number 5: trigonal-bipyramidal and square-pyramidal. Trigonal-bipyramidal and square-pyramidal geometries are common in the case of complexes of metal ions of coordination number 5. Examples of trigonal-bipyramidal complexes are $[CuCl_5]^{3-}$, $[Fe(CO)_3(PF_3)_2]$, and $[Mn(CO)_4NO]$. Examples of square-pyramidal complexes are $[Ni(CN)_5]^{3-}$ and $[CoCl(dppe)_2]^+$.

Coordination numbers 7, 8, and 9: various. Further types of coordination geometry exist for large cations, especially those of the 31 lanthanide cations, for example, $[Ho(acac)_3H_2O]$, $[NbF_7]^{2-}$, $[Mo(CN)_8]^{4-}$, and $[ReH_9]^{2-}$.

oxidation state zero: condition characterized by an atom having neither lost nor gained electrons

dppe = $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$; a bidentate neutral molecule that coordinates through the two phosphorus atoms.

Carbonyls and Organometallic Compounds

Carbonyl compounds and organometallic compounds are two groups of coordination compounds in which carbon atoms are bonded to the metal center. In neutral carbonyls, carbon monoxide molecules are bonded to the metal atom, which is often in **oxidation state zero**. Examples of neutral carbonyl compounds are $[Ni(CO)_4]$ (tetrahedral); $[Fe(CO)_5]$ (trigonal-bipyramidal); and $[Mo(CO)_6]$ (octahedral).

Probably the most famous of the organometallic compounds is the exceedingly stable orange ferrocene, $[Fe(C_5H_5)_2]$. Its discovery in 1951 triggered an explosion in **coordination chemistry**, and the subsequent preparation of thousands of new organometallic compounds. Ferrocene consists of two planar, five-membered rings sandwiching an iron atom between them. Moreover, the bonding in organometallic compounds follows the same rules as the bonding in the carbonyls. The metal atom accepts electrons from the ligands until it achieves a valence electron count of 18 (the number of valence electrons in an atom of the nearest **inert** gas). This is called the Effective Atomic Number (EAN), or **eighteen-electron rule**, first stated by Nevil Sidgwick in 1927 for the metal carbonyls in which each CO group donates two electrons to the metal atom to form an M–C bond. Some examples of the rule are: $Ni(CO)_4$, **atomic number** of Ni = 28, atomic number of Kr = 36, 8 electrons are required, thus 4 CO groups are attached in a tetrahedral arrangement; $Re_2(CO)_{10}$, atomic number of Re = 75, atomic number of Rn = 86, 11 electrons are required for each Re atom. Five CO groups contribute ten electrons, the eleventh comes from sharing a pair of electrons in a Re–Re metal–metal *sigma* bond, giving octahedral geometry about the Re atom.

coordination chemistry: chemistry involving complexes of metal ions surrounded by covalently bonded ligands

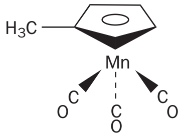
inert: incapable of reacting with another substance

Eighteen Electron Rule: rule noting that coordination complexes with eighteen electrons are stable; electrons from both metal species and ligand donor species are counted

atomic number: the number assigned to an atom of an element that indicates the number of protons in the nucleus of that atom

In ferrocene, each **cyclopentadienyl ring** is considered to donate five electrons to the iron atom, atomic number = 26, giving a total of 10 + 26 = 36 electrons, the atomic number of krypton. Similarly, bonding in the compound $[Mn(CO)_3(C_5H_4–CH_3)]$ obeys the EAN eighteen-electron rule.

cyclopentadienyl ring: five-membered carbon ring containing two C–C double bonds; formula C_5H_6



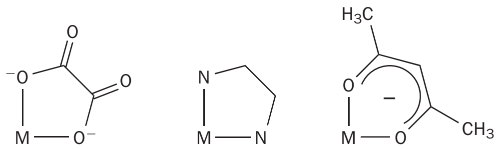
$[Mn(CO)_3\ (C_5H_4—CH_3)]$

The atomic number of Mn = 25; 25 + 5 + (3 × 2) = 36 electrons: the rule is satisfied. This mixed cyclopentadienyl carbonyl complex is of importance as an antiknock compound in gasoline.

Chelating Ligands

EDTA. The bidentate ligands ethylenediamine, oxalate anion, and acetylacetonate anion form **chelate** complexes of enhanced stability, due to the formation of inflexible five- or six-membered rings with the metal.

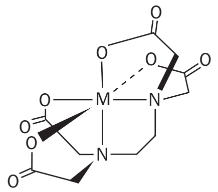
chelate: Greek for "claw"; compounds that have two or more ligand atoms that can attach to metal ions.



Bidentate ligands forming five- and six-membered rings

The compound ethylenediaminetetraacetic acid, on deprotonation, is the hexadentate tetraanion ligand EDTA, which forms remarkably stable complexes by simultaneously bonding through the two nitrogens and four oxygens, one each from the four acetate groups. EDTA is used in toilet soap as a water-softener, in bread as a preservative, and in underarm deodorants as a deodorizer. The magnesium derivative [MgH_2EDTA] is used to treat patients suffering from heavy metal poisoning. EDTA removes the active cation (M^{2+} or M^{3+}) by "engulfing" it to form a water-soluble octahedral complex, which is readily **excreted**.

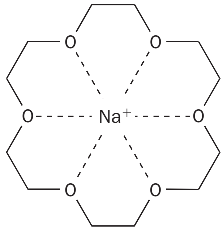
excrete: to eliminate or discharge from a living entity



Chiral complex [MEDTA]

The anion D2EHPA, derived from di(ethylhexyl) phosphoric acid, forms a strongly held four-membered {$M^{2+}O_2P$} ring.

Macrocyclic ligands. Cations of the group one metals form stable complexes with macrocyclic polyethers, for example, Na^+ and "18–crown–6," (–O–CH_2–CH_2–)$_6$.



Macrocylic complex [$Na^+\cdot$18-crown-6]

The ultimate in encapsulation of a metal cation occurs by ligands termed *cryptands*, for example, $N(CH_2–CH_2–O–CH_2–CH_2–O–CH_2–CH_2)_3N$, which completely encapsulates the cation; the complex with the K^+ cation is 1,000 times more stable than the corresponding Na^+ complex. The preparation and study of these compounds, by Donald J. Cram, Jean-Marie Lehn, and Charles J. Pedersen, earned them the Nobel Prize in chemistry in 1987.

Bonding and Stability

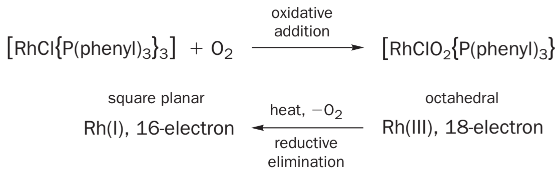
The strength of the metal–ligand bond ranges from the weak ion-dipole interaction between Mg^{2+} and the O atom of the water molecule in $[Mg(H_2O)_6]^{2+}$ (in Epsom salts), to the very strong bonding in the $[Fe(CN)_6]$ units in the pigment Turnbull's blue, to the metal–C **covalent bonds** in organometallic compounds. The colors and magnetic properties of transition metal complexes can be explained by crystal field theory, while the metal–ligand covalent bonding is described by the molecular orbital approach.

covalent bond: bond formed between two atoms that mutually share a pair of electrons

The metal atom in the square-planar complexes of Pd(II), Pt(II), Rh(I), Ir(I) has only sixteen electrons in its valence orbitals. These complexes are easily oxidized by the addition of oxygen or halogens to yield an octahedral complex that obeys the EAN (eighteen-electron) rule. When heated, the 18-electron complex loses the diatomic molecule and the metal is reduced to the 16-electron complex. This cycle is important in **homogeneous catalysis**.

homogeneous: relating to a mixture of the same materials

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



Homogeneous Catalysis

Coordination complexes serve as catalysts in several important industrial reactions. In the Oxo reaction, $Co_2(CO)_8$ reacts with H_2 to form $HCo(CO)_4$, which catalyzes the addition of H_2 and CO to olefins to give aldehydes. Wilkinson's **catalyst**, [RhCl{P(phenyl)$_3$}$_3$], is a catalyst used for the hydrogenation of alkenes, especially important in the manufacture of pharmaceuticals because it is very selective and is effective under mild ambient comditions. Polyethylene is produced from ethylene at low pressure by using $TiCl_4/Al(C_2H_5)_3$ as a catalyst; for developing this process, Karl Ziegler and Giulio Natta earned a Nobel Prize in 1963.

catalyst: substance that aids in a reaction while retaining its own chemical identity

Extractive Metallurgy

The extraction and purification of the valuable metals by hydrometallurgical processes are totally dependent on the formation of stable coordination compounds. A few examples are

palladium: *trans*$[Pd(NH_3)_2Cl_2]$
platinum: $[PtCl_6]^{2-}$
gold: $[Au(CN)_2]^-$ and $[AuCl_4]^-$
uranium: $[UO_2(SO_4)_3]^{4-}$
cobalt: $[Co(D2EHPA)_2]$

The neutral cobalt D2EHPA complex is unique in its being soluble in kerosene, a property that makes possible the industrial solvent extraction process.

Bioinorganic Systems

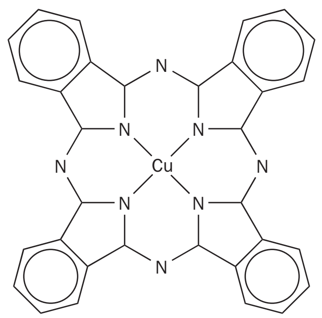
Coordination compounds play important roles in nature. **Chlorophyll**, which is involved in **photosynthesis** in plants, is a coordination complex of magnesium. Hemoglobin, the oxygen transporter in the human body, is a coordination complex of iron. **Vitamin** B_{12}, necessary for the prevention and cure of pernicious anemia, is a coordination complex of cobalt. In all three compounds, the metal ion is in an approximately octahedral environment, its coordination number is 6, and bonded to it are the four nitrogen atoms of a planar **porphyrin**-like ring. The basic planar ring structure is closely related to that of the extremely stable blue pigment, Cu(II)phthalocyanine.

chlorophyll: active molecules in plants undergoing photosynthesis

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

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

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 covalent bonds



Copper phthalocyanine complex

All metals will form coordination compounds. The stability of a coordination compound depends on the nature of the ligands and the atomic number and oxidation state of the metal. SEE ALSO BONDING; CHEMOTHERAPY; WERNER, ALFRED.

Michael Laing

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29
Cu
COPPER
65.34

Copper

MELTING POINT: 1,084.62°C
BOILING POINT: 2,927°C
DENSITY: 8.96 g/cm^3
MOST COMMON IONS: Cu^+, Cu^{2+}

Copper was first used by humans more than 10,000 years ago. A copper pendant discovered in what is now northern Iraq has been dated to about 8700 B.C.E. For nearly five millennia copper was the only **metal** known to humans. Early copper artifacts—first decorative, then utilitarian—were undoubtedly hammered out from "native copper," pure copper found in con-

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

junction with copper-bearing ores in a few places around the world. By 5000 B.C.E., the dawn of **metallurgy** had arrived, as evidence exists of the **smelting** of simple copper oxide ores such as malachite and azurite.

metallurgy: the science and technology of metals

smelting: process by which ores are reduced in the production of metals

Known worldwide copper resources are estimated at nearly 2.6 trillion kilograms (5.8 trillion pounds), of which only about 12 percent (300 billion kilograms; 804 billion pounds) has been mined throughout history. Nearly all of this mined copper is still in circulation, as copper's recycling rate is higher than that of any other engineering metal.

As a molten liquid, copper may be poured to form cake or slabs from which plate, sheet, strip, and foil are rolled; billet or logs from which tube, rod, bar, and forgings are extruded; wire rod from which wire is drawn; and ingot or bricks from which copper may be alloyed with other metals or used by foundries for casting.

There are more than 450 copper **alloys**, including brasses, bronzes, copper-nickels, nickel-silvers, and other specialty alloys. Copper is naturally a salmon color and may oxidize or patinate to gradually become dark brown or a greenish blue. Its alloys may range from pink to brown to gold to silver in color.

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

Copper is used extensively for its high thermal and electrical conductivity and corrosion resistance. In the United States, the most predominant of thousands of copper and copper alloy applications include building construction (largely sheet, tube, building wire, and hardware), 45 percent; electrical and electronic products, 26 percent; transportation equipment, 9 percent; industrial machinery and equipment, 10 percent; and consumer products, 10 percent. SEE ALSO ELECTROCHEMISTRY.

Ken Geremia

Internet Resources

Copper in Your Home. Available from <http://www.copper.org/copperhome/homepage.html>.

The Copper Page. Available from <http://www.copper.org/>.

The Standards & Properties for Copper and Copper Alloys. Available from <http://properties.copper.org/>.

Cori, Carl and Gerty

AMERICAN BIOCHEMISTS
1896–1984 (CARL) 1896–1957 (GERTY)

Carl and Gerty Cori were a husband-and-wife team who worked closely together on research into carbohydrate metabolism.

Carl and Gerty were born in Prague, Czechoslovakia, and met as students at the German University of Prague where they both earned medical degrees in 1920. They were married that same year and migrated to the United States in 1923, both joining a research institute in Buffalo, New York. They became naturalized citizens of the United States in 1928.

In 1931 Carl accepted a position as professor of biochemistry at Washington University Medical School in St. Louis and Gerty was appointed as a research associate. She eventually achieved the rank of professor of biochemistry in 1947. The focus of their research was carbohydrate (sugar) metabolism and the influence of various hormones on these metabolic pathways.

American biochemists Gerty Therese Radnitz Cori and Carl Ferdinand Cori, co-recipients of the 1947 Nobel Prize in physiology or medicine, "for their discovery of the course of the catalytic conversion of glycogen."

In 1936 they discovered the previously unknown metabolic intermediate glucose-1-phosphate, known as the "Cori ester." (See Figure 1).

Research into the formation of this ester demonstrated that it was formed from glycogen, a polymer of glucose employed by many living system as way to store energy. Over the next few years the Coris demonstrated the existence of a new enzyme, polysaccharide phosphorylase, which catalyzes both the formation of glucose-1-phosphate from glycogen and the reverse reaction in which glucose-1-phosphate is incorporated into glycogen; they also succeeded in purifying the enzyme. Since many enzyme-catalyzed reactions are reversible, demonstration of the pathways required ingenious use of selective enzyme inhibitors that permitted the Coris to demonstrate distinct reactions and isolate the enzymes carrying out the reactions. They eventually linked the formation of glucose-1-phosphate from glycogen in the liver to the transport of glucose to muscle cells where, under anaerobic conditions, glucose can be used as an energy source resulting in the formation of lactic acid. The lactic acid can then be transported back to the liver and, through a series of reactions, be used to reform glycogen. This pathway is known as the Cori cycle. The importance of the Coris's work was recognized when they received the Nobel Prize for physiology or medicine in 1947.

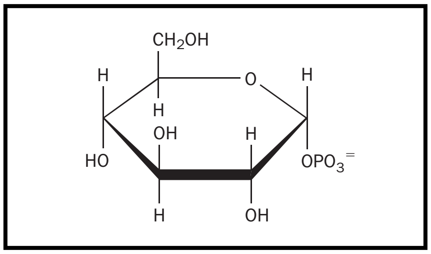

Figure 1. Structure of the Cori ester.

The Coris were also noted for their work investigating the influence of various hormones on carbohydrate metabolism. For example, they demonstrated that epinephrine, a hormone released by the adrenal gland, stimulates the formation of an enzyme that forms glucose from glycogen. They also discovered that insulin stimulates the enzyme hexokinase, which promotes the formation of glycogen from glucose and that a hormone released by the pituitary inhibits the activity of this enzyme. For this and other work the Coris received the Squibb Award in Endocrinology; Gerty was awarded the Garvan Medal of the American Chemical Society as well as a number of other awards and prizes.

After Gerty's death in 1957, Carl continued his work on the mechanism of enzymes involved in carbohydrate metabolism and remarried in 1960. He continued to publish the results of his research into the early 1980s until shortly before his death in 1984. SEE ALSO ENZYMES; KREBS CYCLE.

Robert K. Griffith

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Corrosion

Corrosion is the deterioration a material undergoes as a result of its interaction with its surroundings. Although this definition is applicable to any type of material, it is usually reserved for metallic **alloys**. Of the 105 known chemical elements, approximately eighty are **metals**, and about half of these can be alloyed with other metals, giving rise to more than 40,000 different alloys. Each of the alloys will have different physical, chemical, and mechanical properties, but all of them can corrode to some extent, and in different ways.

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

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

Corrosion is a natural phenomenon. When newly made steel is first exposed to the air, its originally shiny surface will be covered with rust in a few hours. The tendency of metals to corrode is related to the low stability of the metallic state. Metals occur either in the pure metallic state, the zero **oxidation** state, or in the form of compounds with other elements (they acquire positive states of oxidation). In the natural world, most metals are found as compounds with other elements, indicating the greater stability of their oxidized forms. For this reason, to obtain the pure metal from one of its compounds, it is necessary to put in energy. The reverse is true when a metal is exposed to its environment: it tends to release this stored energy through the processes of corrosion. This is rather analogous to what happens when an object is suspended at a point above the ground (equivalent to the metallic state). When allowed to fall or reach a stable state, it returns to a position of minimum energy on the ground (equivalent to the metal's oxidized state).

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

The chemical reactions that take place in corrosion processes are reduction-oxidation (redox) reactions. Such reactions require a species of material that is oxidized (the metal), and another that is reduced (the oxidizing agent). Thus the complete reaction can be divided into two partial reactions: one, oxidation; the other, reduction. In oxidation, the metal loses electrons. The zone in which this happens is known as the anode. In the reduction reaction, the oxidizing agent gains the electrons that have been shed by the metal, and the zone in which this happens is the cathode.

This metal bolt is rusted, a result of the oxidation of the iron metal of which it is composed.

galvanic: relating to direct current electricity especially when produced chemically

Corrosion processes not only influence the chemical properties of a metal but also generate changes in its physical properties and its mechanical behavior. This is why the effects of corrosion are manifested in a variety of forms. The most common form is uniform corrosion, whereby there is a generalized, overall "attack" of the entire exposed surface of the metal, leading to a more or less uniform reduction in the thickness of the affected metal. In contrast, there is the process of localized corrosion, in which an intense attack takes place only in and around particular zones of the metal, leaving the rest of the metal unaffected; an example is pitting corrosion. Some other forms of corrosion are stress corrosion cracking, **galvanic** corrosion, selective alloy breakdown, intergranular corrosion, fatigue, friction, erosion, cavitation, hydrogen enbrittlement, biocorrosion, and high temperature oxidation.

It is easy to find everyday objects that show signs of corrosion. A used automobile consists essentially of different metals, plastics, paints, metallic coatings, and so forth, which have been exposed to a variety of aggressive conditions. These materials are exposed to the action of atmospheric agents under conditions of high temperature, are incorporated in closed water circuits, or are subject to mechanical wear. As a result, we see many signs of corrosion in cars, chiefly on the bodywork and in the exhaust system, and especially after years of use.

Traffic signs, streetlamp standards, metal barriers and fences, and many other items seen along roads are usually manufactured in galvanized steel (normal mild steel with a zinc coating). On such items it is common to see "white" corrosion (zinc oxide), characteristic of the oxidation of a zinc coating, often with spots of red rust also appearing that indicate that the steel base is being corroded.

The sea and the salty atmosphere are saline media that are highly aggressive to metals. Marine structures such as ships, bridges, and drilling rigs and platforms usually show signs of severe corrosion unless they have been properly protected. Cars kept near oceans show signs of corrosion.

Alloys of copper used in the casting of sculptures, and used externally on some buildings, usually show a greenish coloring that corresponds to a layer of corrosion product known as copper patina that gives some protection against further corrosion.

The degradation of reinforced concrete in buildings is commonly caused by the corrosion of the steel reinforcing bars within the concrete, rather than by the loss of the mechanical properties of concrete.

Corrosion processes affect many areas of human activity in which metal products are used. In general, as levels of economic development increase, so do costs incurred as a result of corrosion. It is estimated that the costs attributable to the corrosion of metallic materials amount to 4 percent of the gross domestic product of the developed countries. And this cost, representing a loss of resources, would be even higher if methods of protection against corrosion were not so widely applied. It is estimated that because of this protection, populations are able to reduce these potential losses by a factor of about 30 percent.

Many methods for preventing or reducing corrosion exist, most of them orientated in one way or another toward slowing rates of corrosion. A series of methods that are based on depositing a layer of a second material on the surface of a metal structure to impede the structure's contact with an aggressive medium have been developed. The most prevalent of these is painting, and a wide range of protective paints is now available. As a general estimate, for every 100 m^2 of exposed metal surface, paint is applied to 90 m^2. Included among these surface covering methods are metallic surface treatments, such as chrome, nickel, and galvanized coatings, and inorganic treatments, such as chromates, anodizing coatings, and phosphate coatings.

Another method of protection uses inhibitors, which are substances added to the liquid medium, again to reduce rates of corrosion. Antifreeze liquids utilized in the cooling circuits of vehicle engines have inhibitor agents incorporated into their formulations in order to reduce corrosion problems.

Cathodic protection is an anticorrosion technique widely used in ships and in buried or submerged pipe work. This method seeks to reduce the rate of corrosion of the structure to be protected by joining it to "sacrificial" anodes. In other words, the structure is joined to another metal (an anode) that corrodes more readily, effectively diverting the tendency to corrode away from the structure.

As an alternative to using metals that must be protected by one or other of the methods described, engineers often have an option to use an alloy selected for having a greater resistance to corrosion caused by its surroundings. But better corrosion resistance usually comes at a higher materials and/or manufacturing cost. Engineers must take into account that the corrosion resistance of any alloy depends on both the medium and the working conditions. Hence, alloys with good resistance in one environment may have poor resistance in another, and their resistance is also likely to vary according to differences in exposure conditions, such as temperature or stress. SEE ALSO Oxygen.

F. Javier Botana

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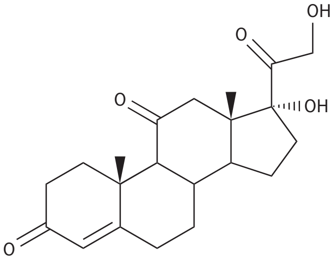
Cortisone

Cortisone is a steroid produced in the adrenal glands of the human body. The isolation of cortisone from the mixture of molecules produced in these glands was carried out by American biochemist Edward Kendall and coworkers. Kendall shared the Nobel Prize in physiology or medicine for this work in which he also helped establish the usefulness of cortisone in the treatment of arthritis.

The isolation of cortisone from adrenal glands is a laborious process, so its widespread utility as a medicine awaited the development of synthetic pathways to its production. Percy Julian was the first scientist to accomplish a commercially viable **synthesis** using protein from soybeans, and since his work an increasing number of applications have been found.



The structure of cortisone is shown above. Like other steroids, the molecule contains four fused rings. It is an example of an anti-inflammatory compound—one that reduces swelling. In many cases, swelling causes pain so the ability to reduce inflammation can be important for pain management, including the case of arthritis. In addition to arthritis, cortisone can be used to treat asthma, dermatological diseases, and tuberculosis and to fight the rejection of organ transplants by the body's immune system. SEE ALSO JULIAN, PERCY; STEROIDS.

Thomas A. Holme

EDWARD KENDALL (1886–1972)

Edward Kendall recognized that symptoms of one type of arthritis decrease in females during pregnancy. He worked to isolate and identify hormones that could be responsible for this occurrence. It was during this search that cortisone was discovered in adrenyl glands. For this scientific breakthrough, Kendall was awarded the Nobel Prize in 1950.

—Valerie Borek

synthesis: combination of starting materials to form a desired product

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Cosmetic Chemistry

The global market for skincare and color cosmetics exceeded 53 billion dollars in 2002. The number of new products brought to market continues to expand exponentially. Cosmetic chemists are always looking for interesting and exotic ingredients that improve skin's appearance and health. A vast array of compounds is required to supply these products. The latest edition of the Cosmetics Toiletries and Fragrance Association (CTFA) Dictionary lists more than 10,000 raw materials. Every year hundreds of new ingredients are added to the list of those that have been used for centuries. Some materials used today can be traced to 11,000 B.C.E. in the animal drawings from the caves of Altimira.

History

The appearance of skin care formulation dates to around 3000 B.C.E. in ancient Egypt. Most concoctions were prepared from natural materials. Cleopatra is said to have bathed in donkeys' milk to keep her skin smooth and supple. One naturally occurring material used by the ancients was red ochre, or iron oxide. Lumps of red ore were formed when iron oxidized or rusted. The red iron oxide was found in burial tombs in ceremonial lip tints and rouge preparations. It was also used to draw the ancient cave pictures of animals, as seen in Altimira, and is still used in many makeup formula-

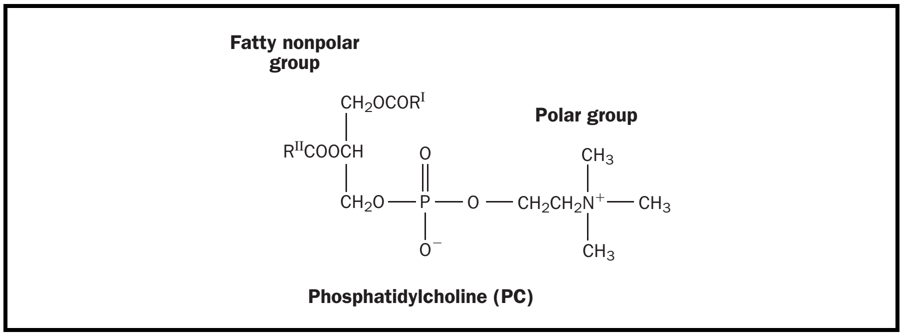


Figure 1. Phosphatidylcholine (PC).

tions today. Eye paints have also been found at ancient gravesites. These paints consisted primarily of a copper-based green ore called malachite that was mined from nearby quarries. Animal fat was combined with fragrant substances such as frankincense and myrrh to produce early skin ointments. More sophisticated creams and lotions were fine tuned through trial and error and passed down over many generations.

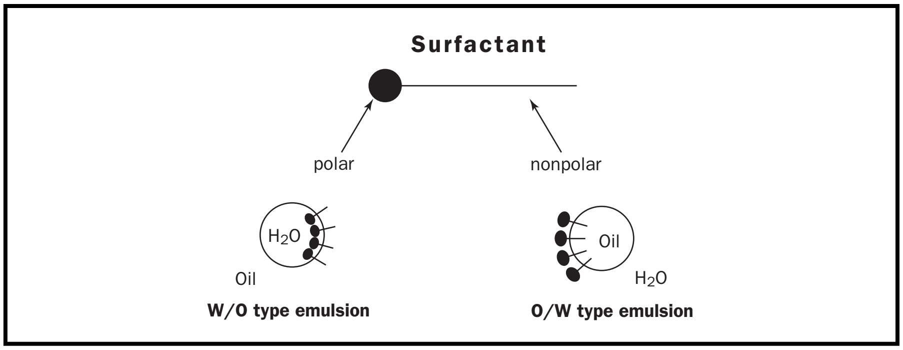
Emulsions

The majority of creams and lotions are emulsions. An emulsion can be defined simply as two immiscible fluids in which one liquid is dispersed as fine droplets in the other. Homogenized milk is an example of a typical oil-in-water (o/w) emulsion. Milk fat (oil) is dispersed in water as fine droplets by the homogenization process. The reason the fat does not float to the top immediately is due to the presence of emulsifiers; in this case, a milk protein called sodium caseinate as well as several phopholipids. In the case of water-in-oil (w/o) emulsions, water is dispersed as droplets and suspended in the oil phase. The nondispersed liquid or external suspending phase is also called the continuous phase. Mayonnaise, vinegar water dispersed as fine droplets in a continuous phase of soybean oil, is an example of a water-in-oil emulsion. Lecithin from eggs stabilizes the mayonnaise emulsion.

Surfactants

Most emulsifiers can be considered surfactants or surface-active agents. These materials are able to reduce the surface tension of water. What makes an emulsifier surface active is related to its HLB, or hydrophile-lipophile balance. HLB is determined by the size of the *hydrophilic* (water-loving or polar) portion of a molecule as compared to the size of the *lipophilic* (oil-loving or nonpolar) portion. The HLB system was created to rank the relative polarity of materials. The most polar, water soluble, materials are at the top of the twenty-point scale with more non-polar, oil soluble, materials closer to zero. The HLB of sodium caseinate is assigned a value of around fourteen because of it's high solubility in water. Lecithin, being poorly soluble in water, has an HLB value of about six. Both have polar groups. The polar group in the milk protein is sodium. Lecithin's surface-active component is a molecule called phosphotidylcholine or PC (See Figure 1). The polar, or water soluble part of PC is the phosphate functional group. The emulsifiers' polar groups orient toward the polar water phase. Their lipophilic, nonpolar groups oriented toward the oil phase to form micelles (see Figure 2). These spherical structures provide stability to the emulsion through Hydrogen bonding and weak electrical forces.

Figure 2. Surfactant.



Skin-care emulsifiers can be divided into two groups based on ionic charge (See Figure 3). Materials that can dissociate into charged species are considered ionic while those that do not are called nonionic. Ionic emulsifiers can be further classified by type of charge. Anionics are negatively charged when **solvated** as in sodium stearate or soap.

solvated: dissolved

When fatty acids are reacted with alkali they form soaps. The process of soap formation is called saponification. The negatively charged stearic acid group is the main emulsifying unit of the soap, giving it the anionic classification. Positively charged emulsifiers are called cationic. Quarternium24's emulsifying unit dissociates into the positively charged ammonium group. Amphoterics are compounds that express both negative and positive charges.

Nonionic emulsifiers are often used in skin-care emulsion for their safety and low reactivity. They are generally classified by chemical similarity. Glycerin, commonly added to cosmetic emulsions for its **humectant** properties, is the backbone of a class of emulsifiers called Glyceryl **esters**. Glyceryl monostearate, or GMS, is called a monoester because of its sole ester linkage (see Figure 4). The diester is prepared by esterifying two molecules of stearic acid for every molecule of glycerin. Glyceryl mono- and diesters are very effective emulsifiers because they contain both polar hydroxyl (OH) groups as well as non-polar fatty acids. If all three of Glycerin's hydroxyl groups are reacted, the resulting triester will have little emulsifying capability.

humectant: moisture retaining

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; a compound with the general formula RC(O)OR′

Stearic acid is called C18 fatty acid. The fatty acids, present in fats and oils, are classified according to their carbon-chain lengths. Because stearic acid is a major component of many of the fats and oils used in beauty treatments, stearate-based emulsifiers are particularly useful. Fatty acids are key components of many cosmetic emulsifiers due their miscibility in a variety of natural and synthetic oils.

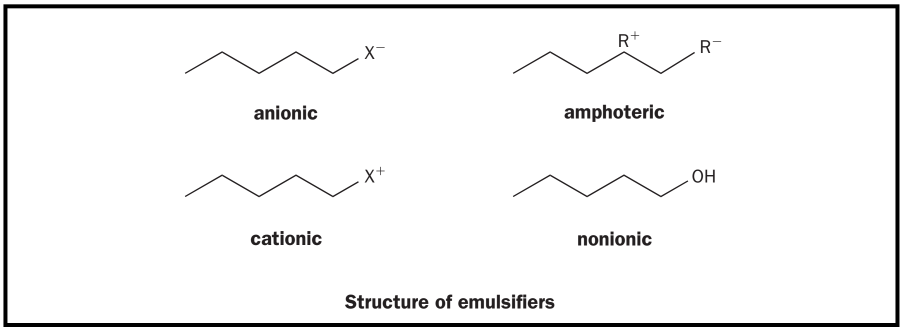


Figure 3. Structures of emulsifiers.

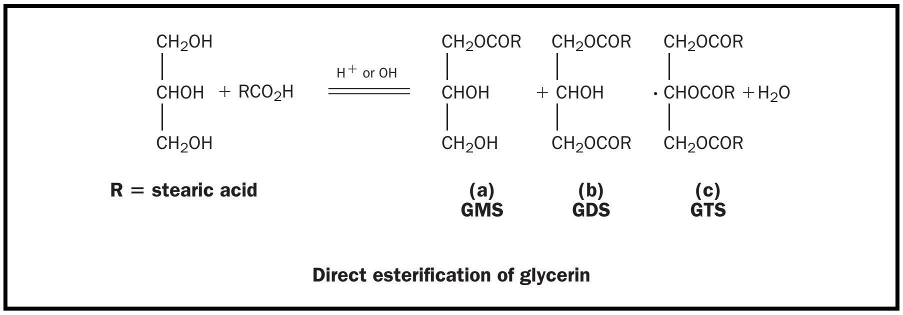


Figure 4. Direct esterification of glycerine.

Esters polyethylene glycol or ethylene glycol are called PEG esters. A PEG ester's solubility is determined by the number of PEG molecules reacted per molecule of acid. PEG 6 oleate for instance has six molecules of PEG reacted with one molecule of oleic acid. As the number of polar, PEG molecules per acid molecule increases the water solubility/HLB is increased; PEG 8 oleate is more soluble than PEG 6 oleate. The cosmetic chemist will often use blends of glyceryl esters and a PEG ester with high and low HLB values to determine the required polarity to emulsify various fats and oils. The many types of emulsifiers are too numerous to list here, however *McCutcheon's Emulsifiers and Detergents* is an excellent source for a more complete listing.

Emollients

The majority of emollients used in personal care and beauty items are fats and oils, also called lipids. Animal fat or tallow is composed primarily of stearic and palmitic acids with carbon chains lengths of 18 and 16 respectively. Many of the major cosmetic companies are moving away from animal-based materials like tallow to renewable vegetable-based materials. Coconut oil and palm kernel oil are often used. Some of the key characteristics required in good emollients are good spreading properties, low toxicity/skin irritation and good oxidative stability. Oleic acid, a major constituent of olive oil has poor oxidative stability due to the presence of its double bond. Fats and oils are considered saturated if they do not have double bonds. Unsaturated oils like olive oil have double bonds that can react with oxygen, especially when heated. The oxidation process can produce off colors and odors in lipids causing them to go rancid and unusable.

Petroleum-based emollients such as petroleum jelly and mineral oil are found in many formulations because they do not contain double bonds or reactive functional groups. Silicone oils such as cyclomethicone, dimethicone are often added to increase slip and emolliency (See Figure 5).

Oils that contain high levels of essential fatty acids, EFAs, are prized for their ability to replenish lipids (oils) that are found naturally within the skin layers. Linoleic acid is an example of an EFA. Long-chain alcohols, also called fatty alcohols, are useful as emollients and emulsion stabilizers. Their polar hydroxyl groups orient to the water phase with their fatty chains oriented towards the oil phase. Esters of fatty alcohols and fatty acids make excellent emollients because of their low reactivity and good stability.

Lanolin, derived from sheep's wool, is often called wool grease. Lanolin has been used for centuries due to it's unique composition of complex sterols, fatty alcohols, and fatty acids. Cholesterol, a cyclic molecule called

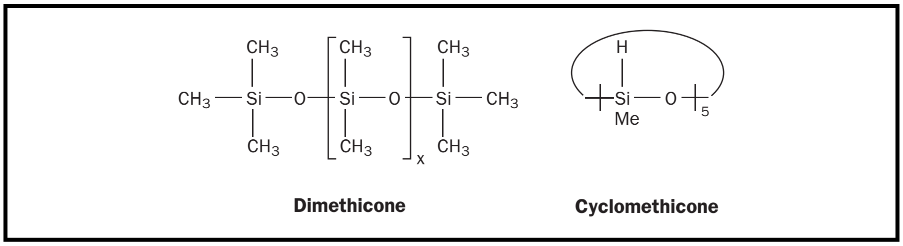


Figure 5. Dimethicone and cyclomethicone.

a sterol, is a major component. The polar hydroxyl groups of sterols and alcohols enable the grease to absorb and hold water. Skin is primarily composed of water, countless oils and emollients are used to nourish and protect it.

Moisturizers

hygroscopic: readily absorb and retain moisture

transepidermal: through the outermost layer of skin

The main distinction between moisturizers and emollients is their solubility in water. Healthy skin requires moisture. Moisturizers are generally polar materials that are **hygroscopic** in nature; they hold onto water. An important tool to assess the efficiency of moisturizers is the high scope. It measures **transepidermal** water loss or TEWL. After a moisturizer is applied to the skin, the moisture level is recorded. After several minutes the moisture level will be reduced due to the natural tendency of the skin to release moisture over time. Ingredients that can maintain a high level of moisture in the upper layers of the skin for several hours can reduce the rate at which water is lost. Glycerin is a very cost-effective ingredient used to help reduce TEWL. Sorbitol, sucrose, glucose, and other sugars are also commonly used to hydrate the skin. Aloe, which contains a mixture of polysaccharides, carbohydrates, and minerals, is an excellent moisturizer. As skin becomes drier in the winter months, it may be necessary to incorporate materials that better seal the moisture in the skin.

Waxes

turbidity: fluidity

Waxes are composed primarily of long-chain esters that are solid at room temperature. Anyone who has ever dipped a finger in molten wax has experienced its sealing properties. Some common waxes used in cosmetics are beeswax, candelilla, carnauba, polyethylene, and paraffin. The melting points of waxes vary widely depending on their unique composition and chain lengths. Commonly used in lip balms and sticks, waxes function as structuring agents, giving the stick enough rigidity to stand up on its own, as well as barrier properties. By combining waxes with different properties such as high shine, flexibility, and brittleness, optimal cosmetic performance can be achieved. Often waxes are combined with compatible oils to achieve the desired softness. Compatibility is generally determined by gauging the **turbidity** and degree of separation of two materials mixed together above their melt points. Waxes are particularly useful in hand creams and mascara emulsions for their thickening and waterproofing properties.

Thickeners

By incorporating enough wax into a thin lotion, a thick cream can be formed. Many thickeners are polymers. Cellulose, a fine powder polymer of repeat-

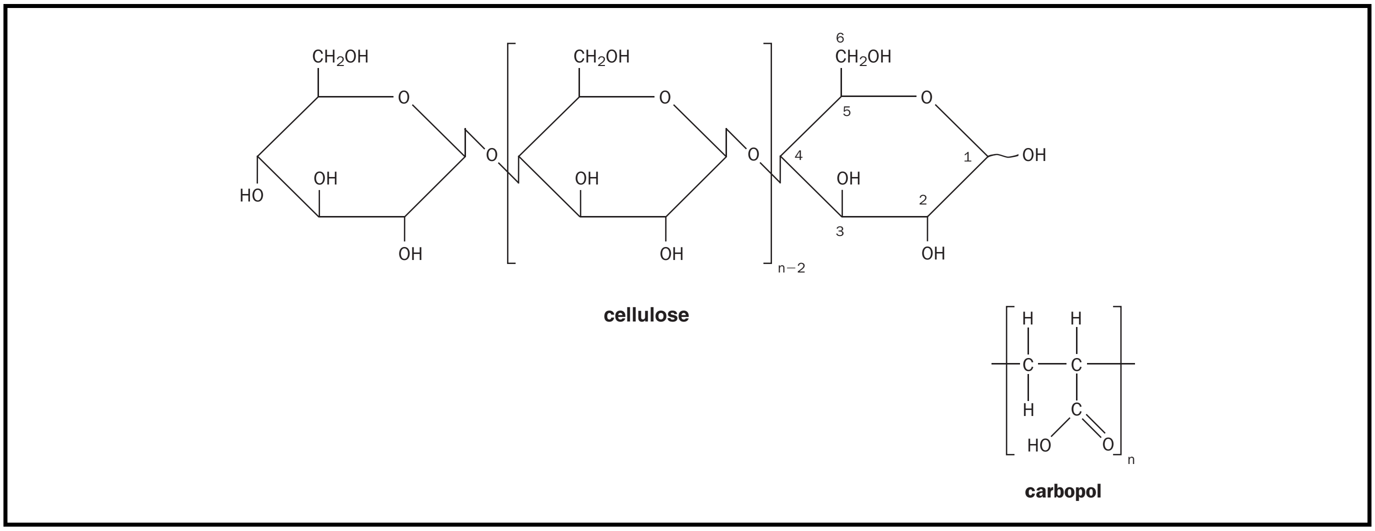


Figure 6. Cellulose and carbopol.

ing D-glucose units, swells in hot water creating a gel network. Carbopol, a polyacrylic acid, swells when neutralized (See Figure 6). Bentone clays swell when their structure, resembling a stack of cards, is opened up through mechanical shear. Carrageenan, pectin, and locust bean gum are all examples of cosmetic thickeners that are also used in some of our favorite foods such as jellies, salad dressings, and pie fillings.

Active Ingredients

Materials that work physiologically within the skin or aid in protecting the skin from insult are also called active ingredients. The term "cosmeceuticals" coined by famed dermatologist Dr. Albert Kligman, refers to a product that is in-between a cosmetic and a drug. Although a cosmetic, by legal definition, can only serve to beautify and protect the surface of the skin, many cosmetic products can be shown to penetrate the dermal layers of the skin to exact a physiological change.

Fruit acids are an example of an active material. Also called alpha hydroxyacids or AHAs, they have the ability to penetrate the skin, where they can increase the production of collagen, elastin, and intracellular substances thus improving the appearance of the skin. Thousands of cosmetic actives are used to affect the skin in a variety of ways. They are used to lighten, tighten, and firm the skin. They can be used to suppress perspiration as in the case of aluminum chlorohydrate. Salicylic acid and benzoyl peroxide are important ingredients because of their anti-acne activity (See Figure 7). Some active materials are added to skin treatments to protect the skin from the environment. Dimethicone and petrolatum are examples of skin protectants.

Sunscreens

Sunscreens are a class of compounds that protect the skin from ultraviolet radiation. Wavelengths between 290nm and 400nm are particularly damaging to the skin. Sunscreens' ability to absorb or reflect these damaging wavelengths are rated by their SPF or sun-protection factor. For instance a person protected with a factor-15 sunscreen will be able to stay in the sun

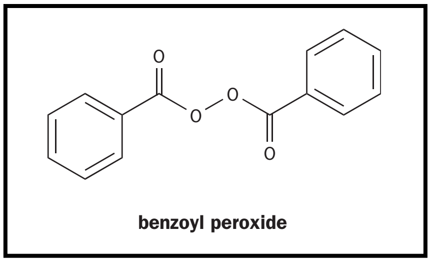


Figure 7. Structure of Benzoyl peroxide.

fifteen times longer than if unprotected. Octyl methoxycinnamate, octyl salycilate, titanium dioxide, and avobenzone are some important topical sunscreens. They can be classified as either UVA or UVB sunscreens depending the wavelengths they absorb. Benzophenone 4, a water-soluble UV filter, is commonly used to protect the color of cosmetic products.

Color

Pigments and dyes are used in products to impart a color. Titanium dioxide (TiO_2) is a white pigment that is mined. In combination with natural mined and synthetic iron oxides, which range in color from red, yellow, black and brown, depending upon the degree of oxidation and hydration, a range of color can be produced that will be suitable for almost every skin tone. Face powders are produced by blending inorganic oxides and fillers. Fillers are inert, generally inexpensive materials such as kaolin, talc, silica, and mica that are used to extend and fully develop colors. Pressed powders like eyeshadows and blushers are prepared by blending additional binding ingredients such as oils and zinc stearate and pressing the mixture into pans.

Eyeshadows and lipsticks often contain pearlescent pigments commonly called pearls. Pearls sparkle and reflect light to produce a multitude of colors. They are prepared by precipitating a thin layer of color on thin platelets of mica. Varying the thickness of the color deposited changes the angle of light refracted though the composite, creating different colors.

Organic pigments are used to color lipsticks and eyeshadows. When organics are precipitated on a substrate they are called lake pigments. The term lake refers to the laking or precipitating of the organic salt onto a metal substrate such as aluminum, calcium, or barium. They are called D&C (drug and cosmetic) and FD&C (food, drug and cosmetic) colors. Some examples are D&C Red#7 calcium lake and FD&C Yellow #5 aluminum lake. Dyes such as FD&C Blue#1 and D&C Yellow #10 are readily soluble as opposed to pigments, which are insoluble. Dyes are useful in providing tints for lotions, oils, and shampoos.

Preservatives

Most cosmetic products require the addition of preservative to prevent microbial contamination and rancidity. Parabens and ester of parabenzoic acid are by far the most commonly used because of their effectiveness against gram-positive bacteria. Phenoxyethanol is used to protect against gram-negative strains. The cosmetic chemist will generally employ a mixture of preservatives to protect against different bacterial strains as well as yeasts and molds. Antioxidants such as tocopherol (vitamin E) and BHT are also added to prevent oxidation of sensitive ingredients as well as protect the skin from free-radical damage.

Conclusion

As long as society continues to puts great emphasis on looking young and beautiful cosmetic chemistry will continue to flourish. A good understanding of the fundamentals of emulsion chemistry and skin physiology are prerequisites, when formulating personal care products. A good cosmetic chemist must be able to combine science and art to create products with the feel and look that consumers desire.

John Castro

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Cottrell, Frederick

AMERICAN CHEMIST
1877–1948

Frederick Cottrell invented the "electrostatic precipitator," which removes pollutants from smoke. Cottrell was born on January 10, 1877, in Oakland, California, the son of Henry and Cynthia Cottrell. His ingenuity and interest in the applied sciences were demonstrated early on. At the age of thirteen, he ran his own printing business with a handpress in the basement of his home, publishing, among other works, a four-page technical magazine, *Boy's Workshop*. He also earned money from odd jobs as an electrician and landscape photographer.

After graduating from Oakland High School, Cottrell attended the University of California at Berkeley. He graduated at the age of nineteen in 1896 with a B.S. in chemistry. He taught high school chemistry for four years and then traveled to Germany, where he earned a doctorate in physical chemistry at the University of Leipzig in 1902. He returned to a teaching appointment at Berkeley, but resigned in 1906 to do independent research on industrial pollution.

A local form of air pollution, the acidic mists from the chimney of a nearby sulfuric acid factory, had triggered Cottrell's interest in this field. Recognizing that fine droplets and solid particles in smoke are held in suspension by the repulsion of electrical charges on their surfaces, Cottrell decided to build a device that could neutralize these charges. The result was a set of probes with a charge of opposite sign that neutralized the charges on the suspended material and caused it to precipitate. The first patent for the electrostatic precipitator was issued on August 11, 1908.

The precipitator was soon at work, removing the acid mist from the stack gases of the sulfuric acid plant. A modification of the original design then removed **arsenic** dust, as well as lead particles, from the emissions of a lead smelter. A further modification precipitated the dust from the emissions of a cement plant.

arsenic: toxic element of the phosphorus group

Cottrell had struggled to finance the experiments that led to the development of the electrostatic precipitator. Although the profits from the eventual manufacture of his precipitator could have made him a wealthy man, he decided that a portion of these monies should go to the support of scientific research. In 1912 he founded the Research Corporation, which is still the recipient of fees from the original patents and distributes them as research grants.

In 1911 Cottrell was appointed chief physical chemist at the U.S. Bureau of Mines, where he rose to the position of director in 1919. He joined the National Research Council (NRC) in 1921, and in 1922 became director of the Department of Agriculture's Fixed Nitrogen Laboratory. He retired in 1930 and devoted the remainder of his life to the Research Corporation. Cottrell died on November 16, 1948, while attending a scientific meeting in Berkeley, California.

Cottrell precipitators continue to benefit the environment by removing particulates from the gases routinely emitted by factory chimneys. Companies that install them find that the devices soon pay for themselves in terms of the value of the materials that are recovered from the precipitated solids.

The Research Corporation continues to benefit the advancement of science through its grants. The organization tends to favor young scientists in need of funds to support their first major projects. As Cottrell himself remarked, "Bet on the youngsters. They are long shots, but many will pay off" (Barker, p.17). Among the recipients of Research Corporation grants were Ernest Lawrence, who developed the cyclotron, for which he received a Nobel Prize in physics, and contributed to the development of atomic energy, and Robert Goddard, pioneer rocket scientist. SEE ALSO LAWRENCE, ERNEST.

Lyman R. Caswell

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Coulomb, Charles

FRENCH ENGINEER AND PHYSICIST
1736–1806

Charles-Augustin de Coulomb was born to affluent parents in Angoulême, France. His father's family was prominent in the legal profession and involved in the administration of the Languedoc region of France. His mother's family was quite wealthy. After being raised in Angoulême, Charles moved with his family to Paris, where he entered the Collège Mazarin and pursued a classical education.

After a brief stay in Montpellier, Coulomb returned to Paris to study at the École du Génie at Mézières. This was one of the first schools of engineering; it specifically focused on military engineering. Coulomb graduated in 1761 with a degree in engineering and the rank of lieutenant in the Corps du Génie. Over the next twenty years, he was posted to a variety of locations where he became involved in the structural design of forts and fortifications, and soil mechanics.

In 1777 his work on torsion balances (among other subjects) won Coulomb a share of the Grand Prix of the Académie des Sciences. Historically, all measurements of weight had been obtained by using a two-pan balance, which is simply a bar centered on a **fulcrum**. Coulomb's **torsion balance** replaced the fulcrum with a fine silk thread or hair, and rather than the up-and-down motion of the pan balance, he used a twist or torsion around this thread. He was able to show that the amount of torsion is proportional to the amount of force; thus he devised a method for measuring very small interactions.

fulcrum: prop or support to an item like a lever

torsion balance: instrument used to measure small forces (weights), based upon the resistance of a wire to be twisted

With his very fine torsion balance, Coulomb was able to demonstrate that the **repulsive force** between two small spheres electrified with the same type of electricity is inversely proportional to the square of the distance between the centers of the two spheres. At the time, the electron had not yet been discovered, so the underlying reason for this remained a mystery but Coulomb was able to demonstrate that both repulsion and **attraction** followed this principle. He was not able to make the quantitative step to show that the force was also directly proportional to the product of the charges, but he did complete some experiments exploring this relationship. As a consequence, the law governing one of the four fundamental forces of nature is named Coulomb's law:

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

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

$$F = kq_1q_2/r^2$$

For his work in setting physics on a course of discovery, the fundamental unit of charge was named the "coulomb" in his honor. SEE ALSO Bonding.

Todd W. Whitcombe

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Cryogenics

Cryogenics is the science that addresses the production and effects of very low temperatures. The word originates from the Greek words *kryos* meaning "frost" and *genic* meaning "to produce." Under such a definition, it could be used to include all temperatures below the freezing point of water (0°C). However, Professor Heike Kamerlingh Onnes of the University of Leiden in the Netherlands first used the word in 1894 to describe the art and science of producing much lower temperatures. He used the word in reference to the **liquefaction** of permanent gases such as oxygen, nitrogen, hydrogen, and helium. Oxygen had been liquefied at −183°C a few years earlier (in 1887), and a race was in progress to liquefy the remaining permanent gases at even lower temperatures. The techniques employed in producing such low temperatures were quite different from those used somewhat earlier in the production of artificial ice. In particular, efficient heat exchangers are required to reach very low temperatures. Over the years the term "cryogenics" has generally been used to refer to temperatures below approximately −150°C.

liquefaction: process of changing to a liquid form

According to the laws of thermodynamics, there exists a limit to the lowest temperature that can be achieved, which is known as absolute zero. Molecules are in their lowest, but finite, energy state at absolute zero. Such a temperature is impossible to reach because the input power required approaches infinity. However, temperatures within a few billionths of a degree above absolute zero have been achieved. Absolute zero is the zero of the absolute or thermodynamic temperature scale. It is equal to −273.15°C or −459.67°F. The metric or SI (International System) absolute scale is known as the Kelvin scale whose unit is the kelvin (not Kelvin), which has the same magnitude as the degree Celsius. The symbol for the Kelvin scale is K, as adopted by the Thirteenth General Council on Weights and Measures (CGPM) in 1968, and not °K. Thus, 0°C equals 273.15 K. The English absolute scale, known as the Rankine scale, uses the symbol °R and has an increment the same as that of the Fahrenheit scale. In terms of the Kelvin scale, the cryogenic region is often considered to be that below approximately 120 K (−153°C). The common permanent gases referred to earlier change from gas to liquid at atmospheric pressure at the temperatures shown in Table 1, called the normal boiling point (NBP). Such liquids are known as cryogenic liquids or cryogens. When liquid helium is cooled further to 2.17 K or below, it becomes a superfluid with very unusual properties associated with being in the **quantum mechanical** ground state. For example, it has zero viscosity and produces a film that can creep up and over the walls of an open container, such as a beaker, and drip off the bottom as long as the temperature of the container remains below 2.17 K.

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

The measurement of cryogenic temperatures requires methods that may not be so familiar to the general public. Normal mercury or alcohol thermometers freeze at such low temperatures and become useless. The platinum resistance thermometer has a well-defined behavior of electrical resistance versus temperature and is commonly used to measure temperatures accurately, including cryogenic temperatures down to about 20 K. Certain semiconducting materials, such as **doped** germanium, are also useful as electrical resistance thermometers for temperatures down to 1 K and below, as long as they are calibrated over the range they are to be used. Such

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

NORMAL BOILING POINTS OF COMMON CRYOGENIC FLUIDS

Cryogen	(K)	(°C)	(°R)	(°F)
Methane	111.7	−161.5	201.1	−258.6
Oxygen	90.2	−183.0	162.4	−297.3
Nitrogen	77.4	−195.8	139.3	−320.4
Hydrogen	20.3	−252.9	36.5	−423.2
Helium	4.2	−269.0	7.6	−452.1
Absolute zero	0	−273.15	0	−459.67

Table 1. Normal boiling points of common cryogenic fluids

secondary thermometers are calibrated against primary thermometers that utilize fundamental laws of physics in which a physical variable changes in a well-known theoretical way with temperature.

The production of cryogenic temperatures almost always utilizes the compression and expansion of gases. In a typical air liquefaction process the air is compressed, causing it to heat, and allowed to cool back to room temperature while still pressurized. The compressed air is further cooled in a heat exchanger before it is allowed to expand back to atmospheric pressure. The expansion causes the air to cool and a portion of it to liquefy. The remaining cooled gaseous portion is returned through the other side of the heat exchanger where it precools the incoming high-pressure air before returning to the compressor. The liquid portion is usually distilled to produce liquid oxygen, liquid nitrogen, and liquid argon. Other gases, such as helium, are used in a similar process to produce even lower temperatures, but several stages of expansion are necessary.

A multicelled human embryo, $2\frac{1}{2}$ days after its removal from a womb. It was cryogenically stored at the Bourn Hall Fertility Clinic, Cambridgeshire, England.

Cryogenics has many applications. Cryogenic liquids like oxygen, nitrogen, and argon are often used in industrial and medical applications. The electrical resistance of most **metals** decreases as temperature decreases. Certain metals lose all electrical resistance below some transition temperature and become superconductors. An electromagnet wound with a wire of such a metal can produce extremely high magnetic fields with no generation of heat and no consumption of electric power once the field is established and the metal remains cold. These metals, typically niobium **alloys** cooled to 4.2 K, are used for the magnets of magnetic resonance imaging (MRI) systems in most hospitals. Superconductivity in some metals was first discovered in 1911 by Kamerlingh Onnes, but since 1986, another class of materials, known as high temperature superconductors, have been found to be superconducting at much higher temperatures, currently up to about 145 K. They are a type of ceramic, and because of their brittle nature, they are more difficult to fabricate into wires for magnets.

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

Other applications of cryogenics include fast freezing of some foods and the preservation of some biological materials such as livestock semen as well as human blood, tissue, and embryos. The practice of freezing an entire human body after death in the hope of later restoring life is known as cryonics, but it is not an accepted scientific application of cryogenics. The freezing of portions of the body to destroy unwanted or malfunctioning tissue is known as cryosurgery. It is used to treat cancers and abnormalities of the skin, cervix, uterus, prostate gland, and liver. SEE ALSO SUPERCONDUCTORS; TEMPERATURE; THERMODYNAMICS.

Ray Radebaugh

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CT Scans

A computed axial tomograph is an axial (cross sectional) view computed from a large set of values, each corresponding to the attenuation of an x-ray beam passed transversely (i.e. in the plane of the desired image) through the subject. In medical applications the subject is a patient; however, applications are not limited to medicine. Computed tomography (fr Greek tomos and graphikos for section or slice and drawing, respectively) has applications in areas as diverse as material sciences, archeology, manufacturing, and facility security.

A CAT Scanner is a machine designed to collect and process the x ray transmission data required to construct and display a computed axial tomograph. "CT scanner" is nearly synonymous with CAT scanner, but recognizes that computed views are not limited to axial views.

Basic physics

photons: a quantum of electromagnetic energy

X rays (comprised of photons) diminish exponentially in intensity as they pass through a material of thickness Δx according to the relationship:

(1) $I_{out} = I_{in}\ e^{-a^{*}\Delta x}$. Where "I" is the intensity, "e" is the Naperian constant, "a" is the attenuation coefficient of the material, and "Δx" is the distance traveled. When "n" adjacent materials are transversed, the formula can be applied repeatedly to yield

(2) $I_{out} = I_{in} * e^{-a_{0*}{}^{\Delta x}} * e^{-a_{1*}{}^{\Delta x}} * e^{-a_{2*}{}^{\Delta x}} \ldots e^{-a_{n*}{}^{\Delta x}}$. Which is equivalent to

(3) $I_{out} = I_{in} * e^{-a_{0*}{}^{\Delta}x_{0}-a_{1*}{}^{\Delta}x_{1}\ -a_{2*}{}^{\Delta}x_{2}\ldots-a_{n*}{}^{\Delta}x_{n}}$, which yields

(4) $^{-}\ln(I_{out}/I_{in}) = a0\Delta x0 + a1\Delta x1 + a2\Delta x2 \ldots an\Delta xn$

Thus the logarithm of the attenuation along any ray is a linear function of the distances traveled through the materials encountered and their respective attenuation coefficients.

Scope of computation

The fundamental computational problem of axial tomography is to solve a group of equations for the attenuation coefficients of each voxel. A voxel —is a volume element, in particular the smallest volume element the system can manage—similar concept to *pixel.* The solution grid is chosen from the points where rays from different rotation angles intersect. After the attenuation coefficients have been determined for the solution grid, averaging and interpolation are used to superimpose a display grid of cubical voxels. For useful resolution, voxels must be small, consequently the system of equa-

A patient is having a CAT scan.

tions becomes very large, i.e., for a resolution of 2mm x 2mm across a body 500mm (19.7 inches) in diameter the minimum number of equations for a solution will be on the order of 64,000 for each transverse slice or "cut." If the detector arc contains 256 detectorsper slice, recordings from about 250 positions around the axis are required. Scanning a region 10 cm long with a corresponding resolution (2mm/cut) will require 50 cuts and the total number of equations becomes 3,200,000. Fortunately mathematicians and computer scientists have been pursuing efficient computational methods for similar problems for decades. A profound improvement was made in 1965 when J. W. Cooley and J. W. Tukey introduced the fast Fourier transform. Present methods require working knowledge of linear algebra, calculus, differential equations, matrices, vector calculus, Fourier transforms, and some programming experience to be appreciated.

By 2002, scans of the resolution and extent mentioned above could be acquired and solved within a few seconds. Consequently the radiation exposure of the patient was limited to safe levels despite the amount of information obtained.

Practical Scanners

A realistic scanner (Figure 1) has a point as the source of x rays. This point produces a wedge-shaped beam aimed at an arc of detectors (possibly more than one layer thick, to acquire data for adjacent cuts simultaneously). The source and detectors have a constant geometric relationship because they are fixed to a rigid ring (gantry). The ring is rotated about the axis of the subject lying on an x ray–transparent table that moves along the ring axis. Exposures are made at many angular positions to acquire sufficient data to compute the voxel values for the cut(s). For the resulting attenuation dataset to be useful it must be recorded with precise values for the corresponding angular position of the beam and the linear position of the table. If slip rings (or telemetry) connect the power, control, and data cables between the

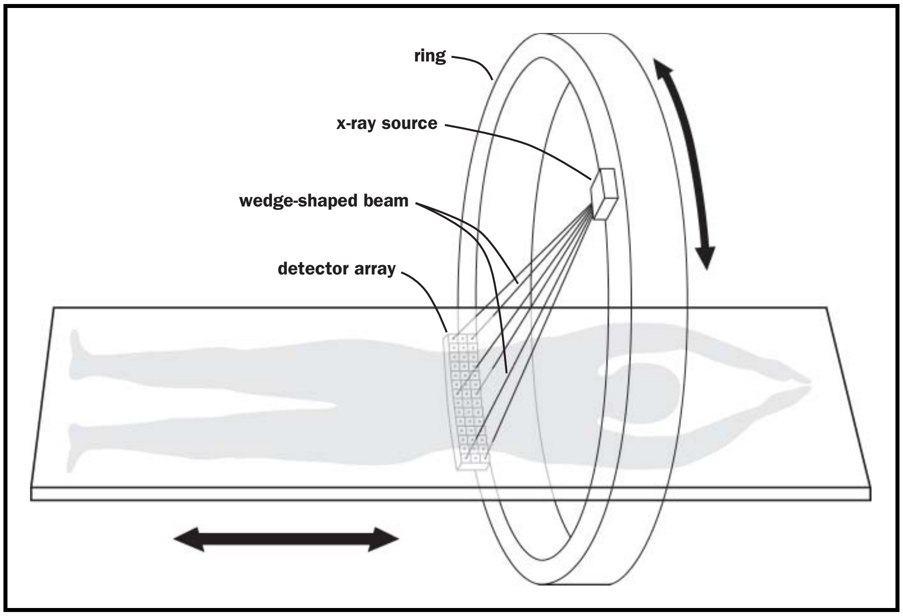

Figure 1. Diagram of a CAT scanner.

ring and the frame, the ring can rotate continuously without reversing between cuts. Continuous rotation with continuous linear table motion of one detector-array-width per ring-revolution produces an aptly named helical scan (loosely called a "spiral" scan). If the detectors and processing electronics are fast enough, rotation, exposure, and detection can also be continuous. The fastest systems can complete a scan of a beating heart so rapidly that there is negligible motion artifact in the computed image—similar to stop action photography with fast shutter speeds and fast film.

History

Austrian mathematician Johann Radon (1887–1956) suspected that images might be created from rays traveling in the plane of a subject and in 1917 presented a proof that this was at least theoretically possible. Decades later, his work proved fundamental in developing methods for computing axial tomographs. CAT scanners could not be built until the late 1960s, as even a rudimentary CAT scanner requires the confluence of imagination and several technologies (just as da Vinci's helicopter had to wait for the invention of the internal combustion engine and light metal alloys).

CAT scanners require affordable computational power, reliable microsized solid state detectors, materials dimensionally stable with respect to time and temperature, high power x ray–source tubes with precisely shaped anodes, and considerable sophistication in computational methods. Similarly, the burgeoning field of computational chemistry would be nonexistent without computational power unattainable until very the end of the twentieth century.

British engineer Sir Godfrey Newbold Hounsfield invented the CAT scanner as soon as it was practical to do so. Beginning in the late 1960s he conceived demonstration conceptual laboratory models that took hours to acquire and analyze data for a single low-resolution slice. Hounsfield was assisted in implementing his ideas by radiologists James Ambrose and

A CAT scan of a human brain with Parkinson's Disease, with visible atrophy.

Louis Kreel. Hounsfield obtained a British patent in 1972 and a US patent in 1976and shared the 1979 Nobel Prize for medicine and physiology, with Allan MacLeod Cormack, a physicist at Yale who had independently developed mathematical methods required to solve the inverse problem of axial tomography.

Refinements

Such a vast quantity of information is collected by high-resolution scanners that additional refinements are needed to help physicians quickly absorb the information. The principal aids are computed color contrasts and images computed from selected viewpoints.

Contrast and Color. The attenuation differences of similar tissues can be enhanced by the administration (intravenously or by mouth) of contrast agents (sometimes called "dyes") that will collect preferentially in one tissue type before eventual elimination by the body. These agents contain salts of heavy atoms, such as iodine, that attenuate x rays more rapidly than living tissue. Even if the attenuation coefficient change might be inapparent to a human viewing a simple gray-level presentation of the data, differences detectable to the imaging system (with or without contrast) permit attenuation coefficients within different ranges to be displayed as different colors:

such as red for blood, pink for muscle, silver for tendon, ivory for bone, and yellow for nervous tissue.

Computed Views. By convention, medical CAT views are oriented with the viewer looking from the feet toward the head with the patient supine. However once the grids of multiple slices have been solved for the attenuation coefficient of each voxel, there are no restrictions except imagination and computation costs on how that information can be presented. Such constructed views actually contain no more information than a series-of-slices presentation, but they can present the information in a way that emphasizes clinically important details. Imagine a rash on the inside of the thorax, this would be very difficult to perceive by mentally integrating the subtle chest wall changes from dozens of slice views. In contrast a computed view looking toward the chest wall from inside the thorax might make the rash obvious. However, only a careful medical history and examination would prompt the physician to request that view from the infinite number of possible computed views.

New applications

endoscopy: a procedure in which an endoscope, comprised of a flexible fiber optic bundle and light source, is passed into the esophagus to examine the wall of the esophagus and the lining of the stomach

Very high resolution systems (voxel diameters of 1 mm or less) may replace exploratory procedures such as endoscopy. The scan data can be processed interactively to give the physician views corresponding to a "virtual" endoscopic examination under his control. However, parallel studies in which hundreds of patients receive literal or virtual visualization procedures with comparison of diagnostic accuracy, and long term outcome will be necessary before virtual examinations can be accepted as the standard of medical care. SEE ALSO Nuclear Magnetic Resonance; Spectroscopy.

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Curie, Marie Sklodowska

POLISH/FRENCH PHYSICIST
1867–1934

Physicist-chemist Marie Sklodowska Curie, sometimes referred to as the "mother of atomic physics," is perhaps the best-known woman scientist of all time—a legend of twentieth-century science. Cowinner of the Nobel Prize in physics in 1903, she was the first person to be awarded a second Nobel Prize, this time in chemistry, in 1911.

French chemist Marie Sklodowska Curie, co-recipient, with Pierre Curie, of the 1903 Nobel Prize in physics and recipient of the 1911 Nobel Prize in chemistry.

Marya Sklodowska was born in Warsaw, Poland, on November 7, 1867. Educated in government schools, she worked for several years in Poland as a governess before going to Paris in 1891 for further study. By dint of considerable effort she completed the physics course at the Sorbonne in 1893, and the course in mathematics the following year. She married physicist Pierre Curie in 1895.

Although her first research focused on the magnetic properties of steel, for her doctoral work she moved to the new field of "radioactivity," as it came to be called. Her studies, a continuation of the work of her teacher, physicist Henri Becquerel, developed directly from Becquerel's 1895 observation that uranium minerals emit rays that pass through opaque materials and fog a photographic plate (as well as discharge an electroscope by making the surrounding air conductive). Marie Curie, with the collaboration of her husband, undertook a systematic investigation of the Becquerel radiation to try to discover its source. Their starting material was the residue left after the extraction of uranium from pitchblende, a uranium ore. The fact that this residue was more radioactive than purified uranium oxide suggested it as a likely source for some unknown material more radioactive than uranium.

Her work at this time was done in minimal facilities that had been secured for her by Pierre Curie at the Paris École Municipale de Physique et de Chimie Industrielle, the industrial college at which he was teaching. With the collaboration, initially, of Gustav Bémont, head of the chemistry section of the École Municipale, she took on the laborious task of isolating the postulated unknown material by chemical methods (group separation and fractional **crystallization**). Pierre Curie established the electrical properties of the rays emitted by the fractions. In June 1898, following their isolation of a fraction 400 times more radioactive than uranium, the Curies reported the presence in the fraction of what was probably a new element. That element, named polonium by Marie Curie, was the first element discovered via its property of radioactivity. Six months later, working with a different fraction, the Curies discovered a second new element. It was given the name radium. In spite of its still impure state, it had an activity a million times that of uranium.

crystallization: process of producing crystals of a substance when a saturated solution in an appropriate solvent is cooled or some solvent is removed by evaporation

In 1902 Marie Curie succeeded in isolating one-tenth of a gram (0.0035 ounces) of pure radium chloride from eight tons of pitchblende residue, a task that required an enormous amount of physical labor. The **atomic weight** of radium she determined to be 225. These results aroused immediate interest. She received her doctoral degree in 1903, her radioactivity investigations forming the major part of her thesis. It was undoubtedly one of the most remarkable doctoral theses ever written. Her Nobel Prize in

atomic weight: weight of a single atom of an element in atomic mass units (AMU) physics, shared that same year with Henri Becquerel and Pierre Curie, received unprecedented press coverage. Pierre Curie was appointed to a professorship in physics at the Sorbonne in 1904. He died suddenly in 1906.

From 1900 until 1904 Marie Curie taught physics at a college for women teachers in the Paris suburb of Sèvres. In 1906, after her husband's death, she succeeded to his professorship in physics, becoming the first woman to hold a teaching post at the Sorbonne. Her scientific research continued, and the tremendous world interest in the new field of radioactivity, coupled with her own international prestige, attracted many students and research workers to her laboratory in the period leading up to World War I. To a notable extent, however, she stepped aside from the increasingly competitive field of atomic physics (which she had in part created) after 1906, and left to others, for example, Ernest Rutherford and his colleagues, the further theoretical development of modern **atomic theory**. Her own work after 1906 tended more toward radiochemistry, and consisted, primarily, of investigations of the radioactive elements (including the substances that came to be called **isotopes**) and their disintegration processes and products. A number of her students and coworkers made notable contributions to both radiochemistry and physics that included: the development of instrumentation for the detection of subatomic particles; characterizations of the range (distance traveled from source) and energy of **α-particles**; descriptions of the effects of α-particles on chemical processes; investigation of β-rays; and the disintegration products in the thorium series. Marie Curie's Nobel Prize in chemistry (1911) was awarded for her discoveries of radium and polonium, and the isolation of radium and the study of its properties.

PIERRE CURIE

Electromagnetic rays emitted by radioactive materials are classifiable into three distinct groups: alpha (α), beta (β), and gamma (γ). Seminal studies by Pierre Curie, the Curie team's major investigator of these rays, include his study of α-rays, his demonstration that β-rays are negatively charged, and his observation (with Marie Curie) that radium causes induced radioactivity.

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

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; an He nucleus

The applications of radiation as a diagnostic tool in medicine were quickly recognized. With the coming of World War I, Curie became director of the Red Cross Radiological Service and worked with her daughter Irène to provide radiology stations for the French army. In 1918 she began work at the new Paris Institute of Radium. She continued to lecture at the Sorbonne until 1934, but gradually turned over the leadership of her laboratory at the Institute of Radium to her daughter and her son-in-law, Frédéric Joliot. By the 1920s she was in poor health. The high doses of radiation to which she had been exposed over the years had taken their toll. Despite failing health, to raise funds for the support of the institute, she made several speaking tours in Europe and the United States. Although never accepted into the Paris Academy of Sciences, she was the first woman elected to the French Academy of Medicine. She died on July 4, 1934, of leukemia, misdiagnosed as tuberculosis, in a nursing home in the Département of Haute-Savoie region of France. SEE ALSO BECQUEREL, ANTOINE-HENRI; POLONIUM; RADIOACTIVITY; RADIUM; RUTHERFORD, ERNEST; THORIUM; URANIUM.

Mary R. S. Creese

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Curium

MELTING POINT: 1,340°C
BOILING POINT: 3,110°C
DENSITY: 13.5 g/cm^3
MOST COMMON IONS: Cm^{3+}

96
Cm
CURIUM
247

The element curium was discovered in 1944 by Glenn T. Seaborg, Ralph A. James, and Albert Ghiorso at the University of California at Berkeley. Its discovery was a result of the bombardment of plutonium-239 (^{239}Pu) with helium ions. Curium was named after the Nobel laureates Pierre and Marie Curie, who were pioneers in the discovery of radioactivity. Although curium is synthetic, minute traces of this element may exist in natural uranium deposits. Curium has ten known **isotopes**, all of which are radioactive. The longest-lived is ^{247}Cm, which has a half-life of 16 million years. Although curium has little use outside of research, ^{242}Cm (half-life 163 days) has been used in isotopic power generators, as it produces about 3 watts of heat energy per gram due to its **radioactive decay**. Curium-245 (^{245}Cm, half-life 8,500 years) is **fissionable**, and can be used as **nuclear** reactor fuel enrichment. Curium was also the **α-particle** source for the Alpha Proton X-ray Spectometer. The physical properties of curium include a boiling point of 1,340°C (2,444°F), and a melting point of 3,110°C (5,630°F). Its density is 13.5 g/cm^3. Curium is very reactive with oxygen, steam, and acids (but not with bases). Several oxides and halides of this element have been prepared. Curium has no known biological uses. If ingested, it tends to accumulate in bone marrow, where it is highly dangerous because its high intensity of radioactivity destroys red blood cells. SEE ALSO Actinides; Actinium; Americium; Berkelium; Californium; Curie, Marie Sklodowska; Einsteinium; Fermium; Mendelevium; Neptunium; Nobelium; Plutonium; Protactinium; Thorium; Uranium.

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

radioactive decay: process involving emission of subatomic particles from the nucleus, typically accompanied by emission of very short wavelength electromagnetic radiation

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

nuclear: having to do with the nucleus of an atom

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

Carolyn J. Anderson

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Internet Resources

Information available from <http://www.chemical elements.com/elements/cm.html>.

Cytosine *See Nucleotide.*

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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